Chapter

Survey of Bauxite Resources, Alumina Industry and the Prospects of the Production of Geopolymer Composites from the Resulting by-product

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Abstract

Guinea is endowed with huge mineral resources. Several geological surveys have identified bauxite, iron, gold, diamond, and several metal ores. Because of the diversity and the magnitude of its resources, the country is referred to *as a geological scandal.* Nowadays the aluminum industry is still at the quarrying stage of bauxite, the main raw material that is converted into alumina and further to aluminum. Approximately 35–40% of the processed bauxite ore goes into the waste as alkaline red mud RM slurry which consists of 15–40% solids. RM and other industrial wastes material such as fly ash FA, rice husk ash RHA, that poses environmental hazards can be mixed to make them apt for usage in engineering applications. Geopolymers GP represent a new class of materials consisting of Al_2O_3—SiO_2-based material suitable for several engineering application. The present chapter presents the bauxitic potential of Guinea, the subsequent developing alumina industry. It reviews the application of RM for the production of geopolymer materials in the perspective of the valorization of the huge bauxite potential of Guinea.

Keywords: bauxite, red mud, silicate, activation, geopolymer, compressive strength

1. Introduction

Bauxite deposits in Guinea are characteristically gigantic and of higher grade than commercial deposits in other parts of the world. Out of Africa's five producer countries, only Guinea has significantly contributed to worldwide production. The only African alumina refinery is located in Fria, Guinea, and has produced about 1% of world output since the start of production in 1960. In the Bayer process for alumina production, huge quantities of the insoluble by-product called red mud RM are generated. Per ton of produced alumina, about 1–1.5 tons of bauxite RM is generated. Management of RM is a first-priority issue for all alumina plants. The high alkalinity is considered to be one of the principal reasons for the limited success until today in finding applications for RM. An application in building materials, as a component in Ordinary Portland Cement (OPC) or geopolymers, seems to

be a straightforward approach in terms of high quantity reuse. Generally, the use of geopolymer as an alternative binder drew the attention because of its excellent properties, such as high compressive strength, resistance to acidic solutions, and thermal stability, in combination with their lower CO_2 footprint [1].

The primary function of a geopolymer is to act as a binder and replace OPC in concrete manufacture or provide complementary products [2]. Some of the advantages that geopolymers have over OPC are their high compressive and flexural strength, their very high temperature resistance, a high resistance to acid, and the ability to utilize multiple waste or byproduct streams [2] Geopolymers binders have the potential to incorporate cations, anions, and organic species within their three-dimensional structure. A significant ecological and marketing benefit reported for geopolymer binder over OPC is the reduction in CO_2; OPC releases 0.55 ton of CO_2 emissions. One ton of CO_2 from the calcination of limestone and the combustion of carbon-based fuel for heat and power generation produces an average additional 0.40 t of CO_2. Comparatively, geopolymer production creates only between 0.2 and 0.5 ton of CO_2 per ton of product, depending on inclusion of life cycle and transport factors [2].

2. Bauxite potential and outlook

Aluminum (Al) is the most plentiful metal in earth's crust, representing more than 7% by weight, and is the third most abundant element after silicon and oxygen. Because aluminum is highly reactive, it is mostly found in oxidized form, of which approximately 250 different minerals exist [3]. Bauxite is the main source of the world's aluminum, supplying 99% of metallic aluminum [1]. Bauxite is a member of the family of lateritic rocks. It is characterized by a particular enrichment of aluminum-hydroxide minerals, such as gibbsite, boehmite and/or diaspore. Bauxite is formed as a weathering product of low iron and silica bedrock. About 90% of bauxite resources in the world can be found in tropical areas while the rest in other latitudes have been exposed to prolonged weathering in their geological past [4]. Bauxite is the principle ore for the production of alumina and aluminum metal. Via a two-stage process that involves the refining of bauxite to alumina by the Bayer process, wet chemical caustic leach process and the electrolytic reduction of alumina to aluminum metal.

2.1 Nature and occurrence

Bauxite is a naturally occurring heterogeneous material and composes of one or more aluminum hydroxide minerals, principally gibbsite [$Al(OH)_3$], boehmite [γ-AlO(OH)] and diaspore [α-AlO(OH)]$_4$. In addition, other compounds are also found in bauxite such as hematite [Fe_2O_3], goethite [FeO(OH)], quartz [SiO_2], rutile/anatase [TiO_2], kaolinite [$Al_2Si_2O_5(OH)_4$] with impurities in traces, as shows **Table 1**. Most commercial bauxite has a minimum Al_2O_3 content of 50–55% [5]. Based on mode of occurrence and parent rock, bauxite deposits can be subdivided into two major groups.

- Alumina-rich or lateritic bauxite, resulting from the weathering of rocks containing alumina.

- *Terra rossa*, occurring as a weathered residue on, or closely associated, with limestone and dolomite. The relatively mobile ions, including alkalis, alkali earths and silica, are leached out leaving a residue of aluminum and iron hydroxides, titania and other insoluble materials

2.2 Bauxite mining and alumina industry in Guinea

Several concepts are used to define the content of a geological deposit: resource, reserve, potential, etc. No matter definitions used, taking into account its identified bauxite deposits both in tonnage and grade, it appears from all studies that Guinea is the country the most endowed with bauxite in the world [6]. The country account for more than one-third of the world's known reserves.

As shows **Table 2** its potential is about 40 billion tons. Its production of bauxite, sourced from three mines located at Sangarédi, Kindia and Fria, is among the largest in the world. At present, crude bauxite and alumina constitute about 60% of Guinea's exports and generate a quarter of its tax revenues [8].

However, Guinea has not realized the full potential of its mineral resources. Annual production of bauxite is very low considering the proven reserves. A comparison of the country's bauxite reserves and production pattern with other major world producers shows that whereas Guinea has the largest known bauxite reserves in the world it has the lowest alumina to bauxite production ratio of all the major bauxite and alumina producing countries. The country has only one alumina refinery plant which has a production capacity of about 0.6 million tons, hence, more than 95% of the bauxite is exported raw. Among others a reason for the poor performance of the sector is insufficient emphasis on local transformation. Power supply constraints and a generally weak investment climate are other possible reasons for low growth in the sector [8]. Power supply, which is vital to production of alumina and aluminum, is a major constraint in Guinea. Poor transport infrastructure and lack of human capital and organizational capacity are also serious concerns. **Figure 1** shows a train transporting bauxite from Débélé (Kindia) on a distance of 130 km to the Port of Conakry.

Name	Composition
Gibbsite	γ-AI(OH_3) α-$Al_2O_3.3H_2O$
(Hydrargillite)	γ-AIOOH, α-AhO].H
Boehmite	γ-AIOOH, α-$Al_2O_3.3H_2O$
Diaspore	α-AIOOH, β-$Al_2O_3.3H_2O$
Hematite	α-Fe_2O_3
Goethite	α-FeOOH
Magnetite	α-Fe_3O_4
Siderite	$FeCO_3$
Ilmenite	$FeOTiO_3$
Anatase	TiO_2
Rutile	TiO_2
Brookite	TiO_2
Halloysite	$Al_2O_3.2SiO_23H_2O$
Kaolinite	$Al_2O_3.2SiO_22H_2O$
Quartz	SiO_2

Table 1.
Main minerals of bauxite deposits [5].

Location	Nr of bowe	Proven and probable reserves	Measured resources	Indicated and supposed resources	Total identified resources and reserves	Extra forecasted resources	Bauxite potential
Boké	94	913	1945	3053	5911	322	8233
Kogon-Tominé	144		2893	7238	10,129	1593	11,722
Fatala	115	62	201	1450	1713	4615	6328
Débélé-Kindia	49	157	23	69	249	126	375
Mali	67		277	225	502	622	1124
Labé	85		320	2225	2545	239	2784
Dalaba-Mamou	57			455	465	859	1324
Donghol-Sigon	49		703	982	1685	272	1957
Balin-Ko	28			927	927		927
Tougué	111	1428	925	1219	3572	791	4363
Dabola	64	617	95	740	1458	855	690
Bafing-Tinkisso	39			89	89	601	
Littoral-Islands*	4	9		39			
Total	894	3178	7, 398	18,686	29,245	10,895	40,139

Exhausted reserves.

Table 2.
Bauxite potential of Guinea (billions of tones) [6, 7].

Figure 1.
Bauxite train of the CBK.

The bauxite and alumina industry is dominated by three producers: Alumina Compagnie de Guinée (ACG), Compagnie des Bauxites de Guinée (CBG), and Compagnie des Bauxites de Kindia (CBK). CBK and ACG are controlled by the Russian aluminum giant RUSAL. CBG is a joint venture between the American aluminum firm Alcoa Inc., the Canadian aluminum firm Alcan Inc., and the government of Guinea. Its main export markets are North America and Europe. These

two corporation networks the Russian possessions (Fria and Débélé) and the US-American and Australian (CBG in Sangaredi and Kamsar) form two business decision spaces that overlay with the official political structure in Guinea.

The alumina refinery plant ACG in Fria converts bauxite into alumina by the Bayer process summarized in as follows.

2.2.1 The Bayer process

The Bayer process is the name for the hydrometallurgical extraction and refinement of alumina from bauxite. Bauxite ore is ground and then digested in highly caustic solutions at elevated temperatures.

$$2NaOH + SiO_2 \longrightarrow Na_2SiO_3 + H_2O \quad (1)$$

$$Na_2SiO_2 + Al_2O_3 \longrightarrow Na_2O.Al_3\ SiO_2 \quad (2)$$

The basic digestion reaction is the following:

$$Al_2O_3.XH_2O + 2NaOH \xrightarrow{135\text{-}145°C} 2NaAlO + (x + 1)\ H_2O \quad (3)$$

Depending on the specific raw mineral:

$$\text{Gibbsite } Al_2O_3.3H_2O + 2NaOH \xrightarrow[(\gamma AI(OH3)]{135\text{-}145°C} 2NaAlO_2 + 4H_2O \quad (4)$$

$$\text{Boehmite } Al_2O_3.H_2O + 2NaOH \xrightarrow[(\gamma AIO.OH)]{205\text{-}245°C} 2NaAlO_2 + 2H_2O \quad (5)$$

$$\text{Diaspore } Al_2O_3.\ H_2O + 2NaOH \xrightarrow[(\alpha AlO.OH)\ \text{High pressure}]{\text{High temper}} 2NaAlO_2 + 2H_2O \quad (6)$$

Crystalline alumina hydrate is extracted from the digestion liquor by hydrolysis.

$$2NaAlO_2 + 4H_2O \longrightarrow Al(OH)_3 + 2NaOH \quad (7)$$

Gangue solids, usually iron oxides, quartz, and other resistant minerals, are separated from the hot sodium aluminate slurry by physical means such as settling and filtration. The solids (red mud and red sand) are countercurrent washed to recover the caustic solutions, then pumped to specially designed impoundment beds. The mud and sand can be intercepted, neutralized, washed, and stored for reuse [2]. The chemical reactions leading to the alumina as final product are given above.

2.2.2 Red mud

According to the composition of the parent bauxite and technology applied for processing, the derived RM contains mainly of different amounts of Fe_2O_3, Al_2O_3, SiO_2, TiO_2, CaO, and Na_2O.

The high alkalinity is considered to be one of the principal reasons for the limited success until today in finding applications for RM. Growing awareness has led to a multitude of studies and semi-industrial trials related to the recycle or valorization

of RM as a raw material for different industrial applications. An application in building materials, as a component in OPC, filler material, or geopolymers, seems to be a straightforward approach in terms of high quantity reuses [1]. Generally, the use of geopolymer as an alternative binder drew the attention because of its excellent properties, such as high compressive strength, resistance to acidic solutions, and thermal stability, in combination with their lower CO_2 footprint [7].

The quantity of alumina produced from bauxite ore depends on the type and the composition of the bauxite ore. Generally authors agree that 1 ton of alumina is produced from 3 ton of bauxite [9]. In average the RM generated per ton of alumina varies between 1 and 1.5 tons, although the amounts from different industrial companies are much broader; it is estimated that over 150 million tons of bauxite residue are produced annually. The quantity of bauxite residue generated at a particular refinery is governed by the processing conditions and bauxite quality [10]. The global inventory of RM stored on land currently is estimated to be over 2.7 billion tons, with an annual growth rate of over 120 million tons.

Over the ACG's 30 years of existence, the quantity of RM produced may very well exceed 20 million metric tons. It should be mentioned that up until the end of the 1980's this mud was simply dumped in the Konkouré river which flows not far from the plant [11].

Figure 2 is a schema allowing the assessment of the accurate amount of alumina and the resulting RM obtainable from crude bauxite.

Bauxite mining and processing have a strong and varied impact on the environment because they entail modifications of the landscape and severe pollution by rejecting wastes into the biosphere (soil, the atmosphere and the water) [13]. Among others RM causes: (i) contamination of water resources with caustic soda and metallic oxide-bearing impurities; (ii) direct contact with fauna and flora;

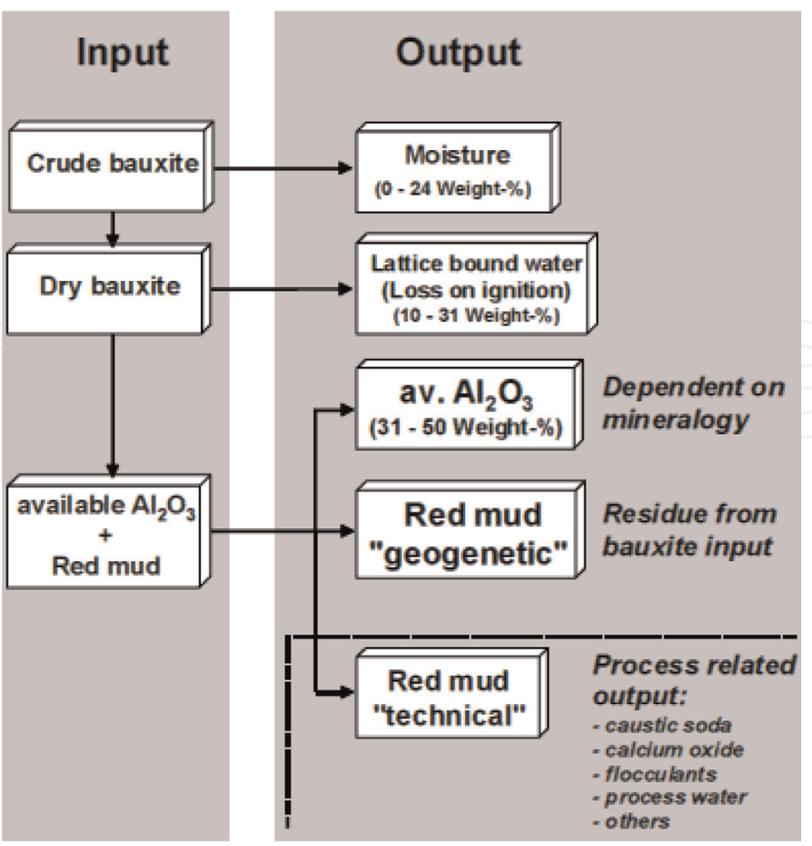


Figure 2.
Calculation scheme for the amount of alumina and red mud that turn out during alumina refinery using chemical and mineralogical data [12].

(iii) evaporation that could originate highly alkaline rainfalls; (iv) visual impact on extensive areas [14].

Chemical analysis shows that red mud contains silicium, aluminum, iron, calcium, titanium, sodium as well as an array of minor elements namely K, Cr, V, Ba, Cu, Mn, Pb, Zn, P, F, S, As and etc. [9]. The variation in chemical composition between red mud worldwide is high. The major chemical composition of red mud for selected countries over the world is presented in **Table 2**. Chemical analysis shows that red mud contains silicon, aluminum, iron, calcium, titanium, sodium as well as an array of minor elements namely K, Cr, V, Ba, Cu, Mn, Pb, Zn, P, F, S. As and etc. The variation in chemical composition between red mud worldwide is high [9]. The major chemical composition of red mud for selected countries over the world is presented in **Table 3**.

ACG plant rejects 1 ton of mud per ton of alumina produced and that each ton of mud contains on average 15 kilograms of caustic soda (NaOH) which has not been recovered by washing [11]. Moreover this mud is composed on average of 60% iron ore (Fe_2O_3), lime ($CaCO_3$) with traces of titanium (TiO_2). **Table 2** shows that RM from ACG/Fria has the highest Fe_2O_3 content and the lowest Al_2O_3 one [10].

2.2.3 Prospects for the valorization of RM

The increasing need of the industry sectors involving aluminum as metal, entailed the improvement of the Bayer process and the subsequent issue of the management of RM. Despite several years of research on the possible valorization of this waste, there is almost no evidence of a large-scale application of this industrial waste to date. Globally research efforts are focused on three fields for the valorization or reuse of RM:

- Civil and chemical engineering applications.
- Mechanical engineering and Metallurgical applications.
- Ecological and biological production purposes.

Country	Plant	Major composition (%)					
		Fe_2O_3	Al_2O_3	TiO_2	SiO_2	NaO_2	CaO
Australia	AWAAK	28.5	24.0	3.11	18.8	3.4	5.26
Brazil	Alunorte	45.6	15.1	4.29	15.6	7.5	1.16
Canada	ALCAN	31.60	20.61	6.23	8.89	10.26	1.66
France	Pechiney	26.62	15.0	15.76	4.98	1.02	22.21
Germany	AOSG	44.8	16.2	12.33	5.4	4.0	5.22
Guinea	ACG/Fria	53.89	14.68	—	7.06	—	2.1
Guinea	Pt Comfort/Texas/US	40	18	—	9.6	2.7	7.6
Italy	Eurallumina	35.2	20	9.2	11.6	7.5	6.7
Spain	Alcoa	37.5	21.2	11.45	4.4	3.6	5.51
Turkey	Seydisehir	36.94	20.39	4.98	15.74	10.10	2.23
UK	ALCAN	46.0	20.0	6.0	5.0	8.0	1.0
USA	RMC	35.5	18.4	6.31	8.5	6.1	7.73

Table 3.
Chemical composition of red mud generated in alumina plants in various countries adapted from [13].

This chapter addresses specifically the use of RM for the production of geopolymers for construction and other engineering applications.

2.2.4 Suitability of RM for the production of GP

A polymer is a macromolecule, organic or inorganic, consisting of the repeated sequence of the same pattern, the monomer (from Greek monos: one or only one, and meros: part), connected to each other by covalent bonds. In the following macromolecule A—A—A—A—A—A—A ... = [—A—]. The constituent unit is A; it is formed of a group of atoms that repeats itself. At the molecular level, most macromolecules are in the form of "long and flexible thread". The chemical reactions allowing to pass from a monomer A to the macromolecule [—A—] are called polymerization.

Geopolymer is a class of inorganic polymers generally formed by the chemical reaction between silica-rich and alumina-rich solids with a high alkaline solution. It is assumed that they result from the dissolution of alumina and silica into a silicate solution occurring the polycondensation of these monomers into aluminosilicate anions.

The general formula of polymer A—A—A—A—A—A—A ... = [—A—] corresponds to M + n [—(SiO_2)z—AlO_2—]n in geopolymer chemistry. A monomer A is equivalent to (—Si—O—Al—O—), poly-sialate-siloxo (—Si—O—Al—O—Si—O—), or poly-sialate-disiloxo (—Si—O—Al—O—Si—O—Si—O—). As shows **Table 2**, the RM from the ACG plant in Fria contains about 15% Al_2O_3. In the chapter below the role of Al_2O_3 as precursor or monomers provider in geopolymerization will be highlighted. Taking into account the country's bauxite reserves and the subsequent quantity of RM resulting from it processing into alumina, geopolymer production may be a serious option for Guinea for the valorization of RM.

3. Geopolymerization

The GP technology has recently attracted increasing attention as a viable solution to reuse and recycle industrial solid wastes and by-products. It provides a sustainable and cost-effective development for many issues where hazardous residues have to be treated and stored under critical environmental conditions [15]. Generally, materials containing mostly amorphous silica (SiO_2) and alumina (Al_2O_3) are a possible source for GP production. Furthermore Geopolymers appear to be a potential alternative to the classic hydraulic binders. Some research studies have been carried on to produce alkali-activated materials from RM. Due to Its low reactivity and low SiO_2/Al_2O_3 molar ratio (<2.0), it has been combined with other higher grade precursors such as metakaolin and metakaolin to prepare alkali-activated materials using sodium hydroxide (NaOH) and sodium silicate as alkaline activators solutions. The authors obtained 10.8 MPa compressive strength after 28 days curing [16].

3.1 Classification of Geopolymers

Bragg used a method based on the theory of distinct silicate or aluminate anions as the basic unit of constitution. This central unit is a tetrahedral complex consisting of a small cation such as Si or Al that lies in tetrahedral coordination with 4 oxygen anions to produce SiO_4 or AlO_4. The silicon-oxygen bond should never be ionic; it should be polar and covalent [5]. This is since specific silicon and oxygen atoms Cannot move at liberty within the crystalline structure. Covalent bonding is more

general and holds for silicates, Al—Si (such as zeolites), alumino-phosphates and geopolymers. Aluminosilicate based geopolymers such as polysialate consist of SiO_4 and AlO_4 tetrahedra which are linked alternatively by sharing all the oxygen atoms [5]. Alkali-activated binders have either amorphous or nanocrystalline microstructures. This depends on the amount of alumino-silicate content in the precursor materials and on the mineralogical nature mineralogy of raw materials [17]. Depending on the composition of the starting materials, alkali-activated binders can be divided into two groups as shows **Figure 3**:

- Alkaline earth binding systems: Me_2O—MeO—Me_2O_3—SiO_2—H_2O, the typical example of this group is alkali-activated blast furnace slag OPC.

- Alkaline binding system: Me_2O—Me_2O_3—SiO_2—H_2O, the typical example of this group is alkali-activated metakaolin or fly ash OPC [3].

Glukhovsky classified the alkaline activators in six groups, where M is an alkali ion: alkalis, MOH; weak acid salts, M_2CO_3, M_2SO_3, M_3PO_4, and MF; silicates, $M_2O.nSiO_3$; aluminates, $M_2O.nAl_2O_3$; aluminosilicates, $M_2O.Al_2O_3$. (2–6) SiO_2 and strong acid salts, M_2SO_4 [18]. Further GP are broadly classified as acid activated and alkali activated geopolymers as shown in **Figure 1**. Acid activated geopolymers were recently introduced, having properties comparable to alkali activated materials e.g. phosphoric acid activated metakaolin produced 30% higher cold crushing strength than their alkali activated counterparts [19]. The higher porosity of this group of polymers suggested their possible application in waste water treatment and as an adsorbent [20]. Acid activated geopolymers have not been explored and further research in this field is required. Alkali activated GP are materials of special interest in the past four decades due to their superior properties compared to OPC. Based on the alumino silicate matrix they are classified as sialate, sialate silaxo and sialate di silaxo.

3.2 Raw materials for geopolymer production

Starting materials are checked for pozzolanic content i.e. $SiO_2 + Al_2O_3$. With the advanced mixing technologies, mix design comprised of pozzolanic and semi pozzolanic waste materials have been reported. The base materials found to be suitable

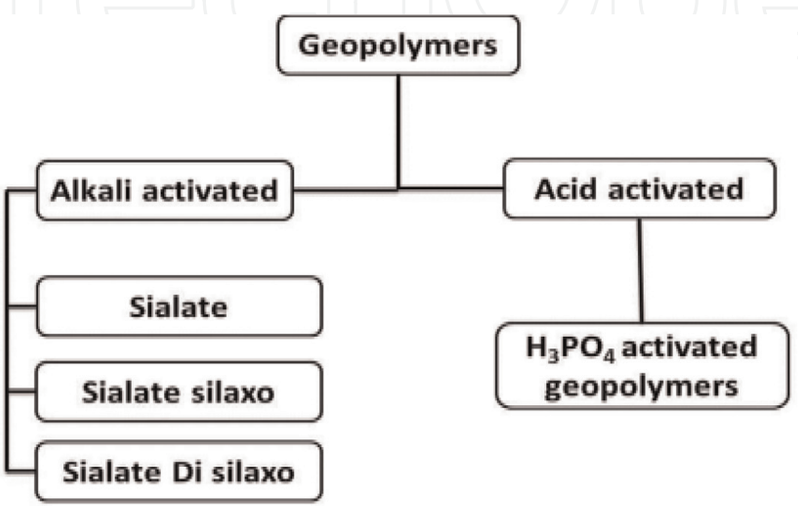


Figure 3.
Classification of Geopolymers [17].

comprise natural minerals such as metakaolin, clays, which contains Si, Al and oxygen in their chemical composition [16]. By-product from other industries such as fly ash, silica fume, slag, rice-husk ash red mud (§ *I.3.1.*), etc. could be utilized alternatively as the source materials. Disposal, price, application and demand of the users are the main factors in the process of the selection of source materials [4].

In order to obtain a GP with desired properties e.g. high strength, low shrinkage, high acid resistance or low cost, a range of ratios need to be controlled: Si/Al ratio; Na/Si and K/Si ratio and water to solid ratio. It is therefore of major importance to characterize the aluminosilicate source and to determine their reactivity, in order to be able to evaluate the amount silicates and aluminates reacting. It should be noted that the particles size distribution or fineness is of importance regarding the reactivity of the aluminosilicate source. The mix can then be optimized by adjusting the type and the amount activators added.

Most of the investigations have used alkali solutions for dissolution of raw materials to form the reactive precursors necessary for geopolymerization. It has been shown that silicate activation increases the dissolution of the starting materials and gives rise to favorable mechanical properties [21].

. Two groups of materials are required to make a geopolymer; one is source materials containing alumina and silica and other is an alkali that activates the polymerization reaction. Basing on their origin materials of the first group are natural or industrial (mainly by-products).

3.2.1 Natural minerals: Kaolinite, calcined kaolinite (metakaolin) and clays

- *Kaolinite (microsilica)*: is a clay mineral having the chemical composition $Al_2Si_2O_5(OH)_4$ Rocks that are rich in kaolinite are known as kaolin or china clay. Kaolinite is a clay mineral with the chemical composition $Al_2S_2O_5(OH)_4$, which means each particle has one tetrahedral silica layer and one octahedral alumina layer [15]. It is a soft, earthy, usually white mineral, produced by the chemical weathering of aluminum silicate minerals like feldspar. Rocks that are rich in kaolinite are known as china clay, white clay, or kaolin. Kaolin is a fine, white, clay mineral that has been traditionally used in the manufacture of porcelain.

- *Metakaolin* is a dehydroxylated form of the clay mineral kaolinite in the temperature range of 500–800°C. It is a highly pozzolanic and reactive material. Kaolinite is a clay mineral with the chemical composition $Al_2Si_2O_5(OH)_4$, which means each particle has one tetrahedral silica layer and one octahedral alumina layer. It is a soft, earthy, usually white mineral, produced by the chemical weathering of aluminum silicate minerals like feldspar.

3.2.2 Industry wastes

- *Fly ash:* fly *ash* is defined as the finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gasses from the combustion zone to the particle removal system. The characteristics of fly ash are loss on ignition (LOI), fineness and uniformity. LOI is a measurement of unburnt carbon remaining in the ash. Finer gradation generally results in a more reactive ash and contains less carbon. Fly ash is a very fine, powdery material, composed mostly of silica. It consists mostly of silt-sized and clay-sized glassy spheres. These are generally spherical in shape and range in size from 0.5 to 100 μm [20]. They consist mostly of SiO_2, which

is present in two forms: amorphous, which is rounded and smooth, and crystalline, which is sharp, pointed and hazardous. Three classes of fly ash are defined by ASTM C 618; Class N fly ash, Class F fly ash, and Class C fly ash [15]. The chief difference between these classes is the amount of calcium, silica, alumina, and iron content in the ash.

- *Red mud*: *RM* (see *§ I.3.1.*) is characterized by strong basicity even with a high water content, because of the presence of huge amount of sodium hydroxide used to extract silicates and alumina. **Figure 4(a)** shows oven dried RM, **Figure 4(b)** grounded RM; its color is due to the Fe_2O_3 or Fe_3O_4, which can make up to 60% of the mass of the RM.

- *Rice-husk ash*: Rice husk is the natural sheath that forms on rice grain during its growth. Removed during the refining of rice, the rice husk ash RHA is generated after burning the rice husk in the boiler. At present, the most common method of disposal of RHA is dumping on waste land, thus creating an environmental hazard through pollution and land dereliction problems. The major compounds from rice husk are silica and cellulose which yields carbon when thermally decomposed [22]. Rice husk is unusually high in ash compared to other biomass fuels, close to 20%. The ash is 92–95% silica, highly porous and light weight, with a very external surface area RHA is an active pozzolan which when combined with line in the presence of water results in a stable and more amorphous hydrate (calcium silicate). Rice husk is unusually high in ash compared to other biomass fuels—close to 20%. **Figure 4(c)** shows RHA after burning of RH at ambient temperature. At higher temperatures the RHA color tends to white and its Si content increases.

This is stronger, less permeable and more resistant to chemical attack. Due to its insulating properties, RHA has been used in the manufacture of refractory bricks. Recently RHA has been incorporated in activated aluminosilicates.

- *Catalyst residues:* Petroleum refineries worldwide process crude oil in fluid catalytic cracking (FCC) units, and 160,000 tons of spent FCC catalyst residue are thus produced every year [23]. The spent catalyst is essentially an agglomeration of zeolite (faujasite) crystals held together by an aluminosilicate matrix including amorphous silica and clays. However, in using this type of residue as a precursor in alkali-activation, it is important to consider the significant heavy metal content of the catalysts, particularly nickel, vanadium and/or lanthanum, as these may impact the performance of the geopolymer materials, and are also potentially leachable under some conditions. Catalysts

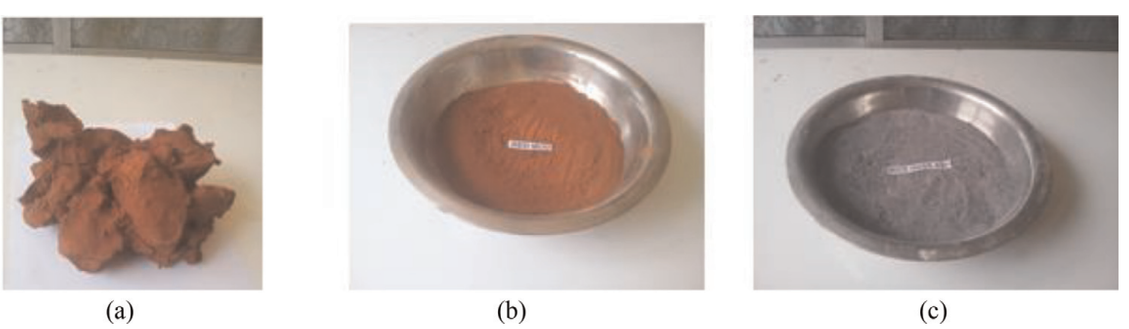


Figure 4.
(a) RM oven dried (b) RM ground (c) rice husk ash.

from different sources and processes also differ in composition and reactivity, meaning that this is rather a diverse class of materials which can provide alkali-activated products with a range of performance levels [24].

- *Ground Granulated Blast furnace Slag (GGBS)*: Ground-granulated blast-furnace slag is obtained by quenching molten iron slag from a blast furnace in water or steam, to produce a glassy, granular product that is then dried and ground into a fine powder [19]. The main components of blast furnace slag are CaO (30–50%), SiO_2 (28–38%), Al_2O_3 (8–24%), and MgO (1–18%). In general, increasing the CaO content of the slag results in raised slag basicity and an increase in compressive strength. The MgO and Al_2O_3 content show the same trend up to respectively 10–12% and 14%, beyond which no further improvement can be obtained [25]. GGBS has now effectively replaced sulfate-resisting OPC on the market for sulfate resistance because of its superior performance and greatly reduced cost.

3.2.3 Particle size and reactivity of raw materials

Particle size of the raw materials is also important factors in geopolymerization. Finer particle sizes of the RHA improve its reactivity and thereby higher degree of geopolymerization can be achieved. The finer the particle size the stronger the geopolymer [26]. Higher degree of geopolymerization makes the resulting geopolymer more ductile and stronger. As the particle size of the RHA decrease the surface area increase [27]. The increased surface area also results in the formation of more ductile and stronger geopolymers. This suggests that the mechanical properties of geopolymers are depending upon the physical property, the particle size of the raw materials. The strength of geopolymer mortars are affected by the fineness of RHA. The increase in the fineness of RHA increases its reactivity and strength of mortars. RHAs with 1– 5% retained on No. 325 sieve are suitable for making geopolymer mortars.

3.2.4 Activating alkali solutions

The efficiency of the alkali activation process of geopolymers is very much dependent on the addition of chemical activators (sodium/potassium hydroxide, soluble silicates, etc.) and also the curing regime (heat treatment) employed on the hardened geopolymer concrete [6]. Strength development of geopolymers fabricated without the addition of chemical activators or subsequent heat treatment is very slow, particularly during the early stages.

The most common alkaline liquid used in geo-polymerization is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate [28].

Besides the aluminosilicate as raw material an alkaline activator is required to produce a geopolymer. The alkali component used as an activator is a compound from the elements of the first group in the periodic table. The common activators can be classified as follows:

- Alkali metal hydroxide: NaOH, KOH, LiOH.
- Alkali metal silicate (AMS) Na_2SiO_3, K_2SiO_3.
- Alkali metal hydroxide silicate: Na_2SiO_3 + NaOH.

- Metal aluminate $NaAlO_2$.
- Metal carbonate Na_2CO_3.

The Alkalinity of the solution is a widely investigated factor and the most significant factor controlling the compressive strength of geopolymer concrete. High alkalinity of the solution accelerates the dissolution of the raw materials, which shortens the setting time. It also enhances the compressive strength of geopolymers. The higher the alkaline concentration is, the higher the compressive strength is obtained.

3.3 Concept and chemical mechanism of geopolymerization

Geopolymer is an inorganic polymer with SiO_4 and AlO_4 tetrahedra being the structural units [29]. Geopolymers composites are also defined as an Al- and Si-rich cementitious, amorphous binder, which is formed by polymerization of an alkali activated solid aluminosilicate precursor [30]. Geosynthesis is based on the ability of the aluminum ion to induce crystallographical and chemical modifications in a silica backbone. Usually polymerization reaction takes place in organic compounds, due to the tetra valancy of the carbon atom. Geopolymerization is an inorganic polymerization. It consists of dissolution and hydrolysis followed by a condensation step in an alkaline silicate plus alumino-silicate system. The chemistry of geopolymerization is similar with the synthesis of zeolites, although the resultant products are different in composition and structure [31]. It consists of chains or a 3D framework of linked AlO_4^{5-} and SiO_4 tetrahedra. The more general term inorganic polymer defines a super group with a deviation from the tetrahedral coordination of Al and Si and the aluminosilicate chemistry [32]. The dissolution of the mineral results with the formation of Si—O—Al species as monomers. Their reorganization leads to the GP network.

The schema below illustrates the reactions proposed for the polycondensation process [12]. In the reactions (8) and (9) the amount of Al–Si materials used depend on the particle size, the extent of dissolution of Al–Si materials and the concentration of the alkaline solution. The formation of $[Mz(AlO_2)x(SiO_2)y{\cdot}MOH{\cdot}H_2O]$ gel is a dominant step in the geopolymerization and essentially relies on the extent of dissolution of aluminosilicate materials (reaction (10)).

$$\text{AI Si material (s)} + \text{MOH (aq)} + Na_2SiO_3\ \text{(s or aq)} \tag{8}$$

$$\downarrow$$

$$\text{AI Si material (s)} + [M_z(AIO_2)_x(SiO_2)\ nMOH.mMOH_2O]\ \text{gel} \tag{9}$$

$$\downarrow$$

$$\text{AI Si material (s)} + [M_a((AIO_2)_a(SiO_2)_b\ nMOH.mMOH_2O] \tag{10}$$

The general empirical formula of geopolymer is as follows:

$$M + n[-(SiO_2)z\text{-}AlO_2\text{-}]n \tag{11}$$

Where M^+ = an alkali cation (K^+, Na^+) for balancing the negative charge of Al^{3+} in IV-fold coordination; n = degree of polymerization; and z = Si/Al ratio. The value of 'z' represents describe the Si/Al ratio, based on which three types can be distinguished: poly(sialate) with 1:1 Si/Al ratio, poly(sialate-siloxo) with 2:1 Si/Al ratio and poly(sialatedisiloxo) with 3:1 Si/Al ratio [7]. Geopolymers possess amorphous to semi-crystalline three dimensional silico-aluminate structures consisting of

linked SiO_4 and AlO_4 tetrahedra by sharing the oxygen atoms, which can be designated as poly-sialate (—Si—O—Al—O—) (Si/Al = 1), poly-sialate-siloxo (—Si—O—Al—O—Si—O—) (Si/Al = 2), poly-sialate-disiloxo (—Si—O—Al—O—Si—O—Si—O—) (Si/Al = 3),and sialate links (Si:Al > 3). The sialate is an abbreviation for silicon-oxo-aluminate. The structures of the above types of poly(sialates) are schematically presented in **Figure 6** [23, 29].

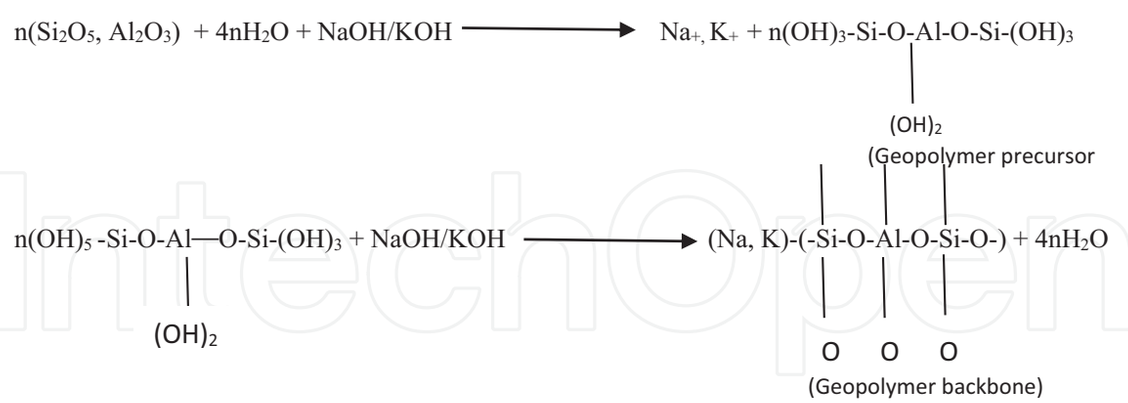
Aluminosilicate backbones are formed during geopolymerization process as shows **Figure 5**. Sialate is an abbreviate form for alkali silicon-oxo-aluminate, the alkali element being (Na, K, Li, Ca) and the term poly(sialate) covers all geopolymers containing at least one (Na,K,Li,Ca)(Si—O—Al) and (Na,K,Li,Ca)-sialate unit. Sodalite frameworks and kalsilite frameworks have structural molecules Na-(—Si—O—Al—O—) and K-(—Si—O—Al—O—) respectively [13]. As shows **Figure 6**, they are chain and ring inorganic polymers that are the result of the polycondensation of the monomer, orthosialate (OH)3—Si—O—Al—(OH).

Sanidine frameworks, K-(—Si—O—Al—O—Si—O—Si—O—) may be considered as the condensation result of orthosialate with two ortho-silicic Si(OH)3 [13]. The sialate unit may be at the beginning, in the middle or at the end of the sequence. There are six isomorphs: 2 linear, 2 branched and 2 cycles. Leucite frameworks with structural molecule K-(—Si—O—Al—O—Si—O—) may be considered as the condensation result of orthosialate with ortho-silicic acid Si(OH). There are three isomorphs, a linear (—Si—O—SiO—Al—O—), mono-siloxo-sialate and 3 cycles. Anorthite frameworks containing 2 sialate unit, Ca-(—Si—O—Al—O—Si—O—Al—O—) are ring polymers that are result of the polycondensation of the monomer [13].

Crystalline alumina hydrate is extracted from the digestion liquor by hydrolysis.

$$2NaAlO_2 + 4H_2O \longrightarrow Al(OH)_3 + 2NaOH \qquad (12)$$

The formation reactions of the above geopolymer material are established by the following two reactions [18].



(13)

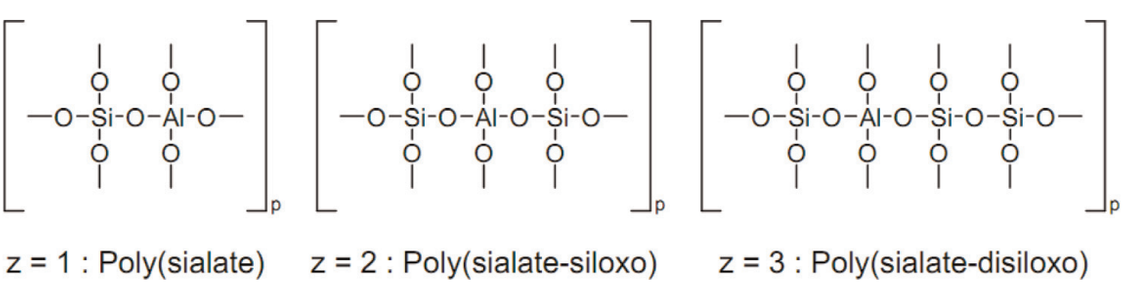


Figure 5.
Schema of GP-monomers units [23, 29].

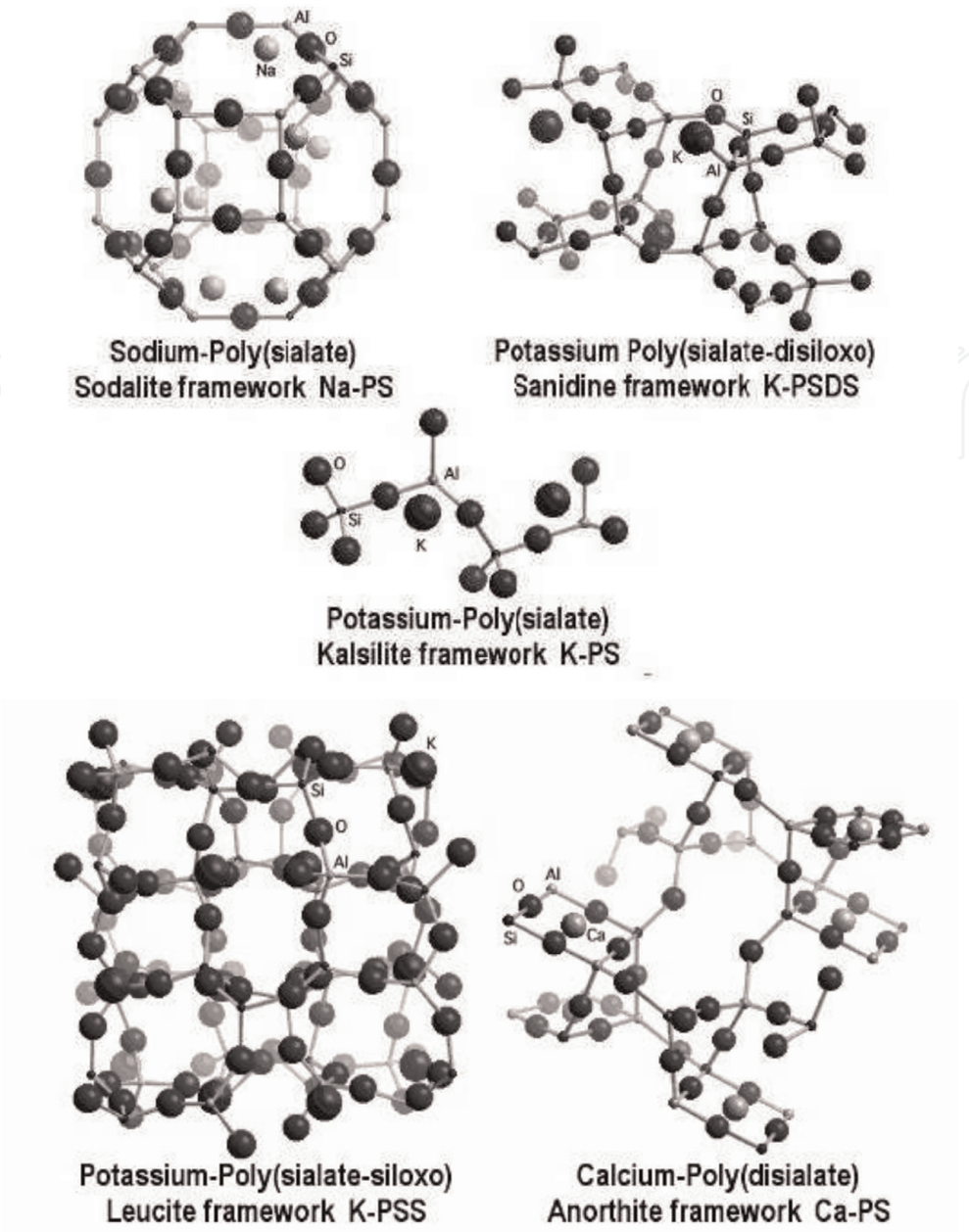
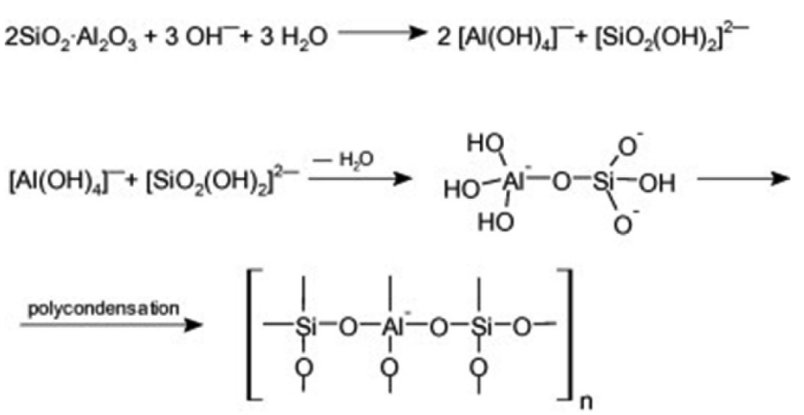


Figure 6.
Polymeric structures from polymerization of monomers [33].

After Duxson, the geopolymer structure consists of cross-linked, SiO_4 and AlO_4-tetrahedral species where the negative charge on Al^{3+} in IV-fold coordination is balanced with the positive charges of the alkali ions (Na+, K+). The geopolymerization reaction can be expressed as shown below:



(14)

Geopolymers are mainly represented in the models proposed by Davidovits and Barboza the as shown in **Figures 7** and **8** [34, 35]. The two models have in common a space, three-dimensional disposition. The Davidovits structural model of GP is designed on the basis of a poly-sialate–siloxo type. It takes on a monolithic type of GP comparable to organic polymers. The water molecules surrounding the Na ion in the Barbosa model suggests the presence of pores in the structure of the GP.

3.4 Characterization of geopolymers

With regard to the characterization of GPs, the use of common materials science techniques presents challenges because of the complex multiphase nature of precursors being structurally disordered: glassy (FA) or thermally disrupted layer (MK). The most widely used tools for microstructural analysis of GP-materials are scanning electron microscopy (SEM), X-ray diffraction (XRD), EDX.

3.4.1 Microstructure of RM and RHA

The SEM diagram of the RM is shown in **Figure 9** RM has relatively porous microstructure with the presence of dispersed particles. The figure presents unequal formed aggregates with smaller particles. The aggregates represent probably Fe_2O_3 particles and needle-shaped particles of Ca_SO_4.

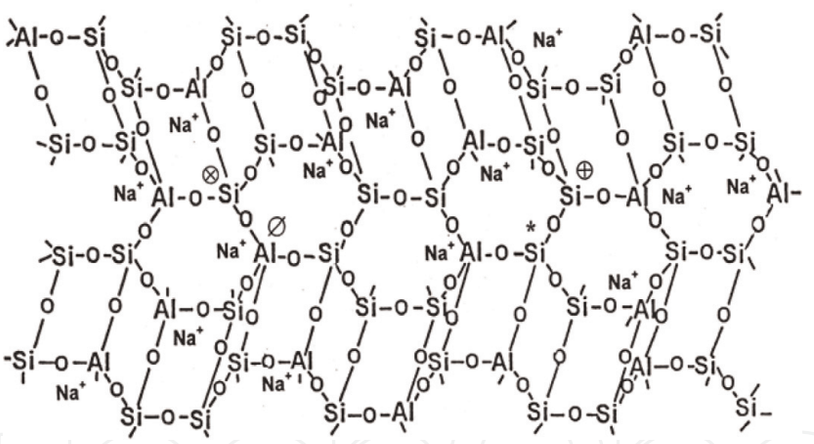


Figure 7.
Davidovits model [34].

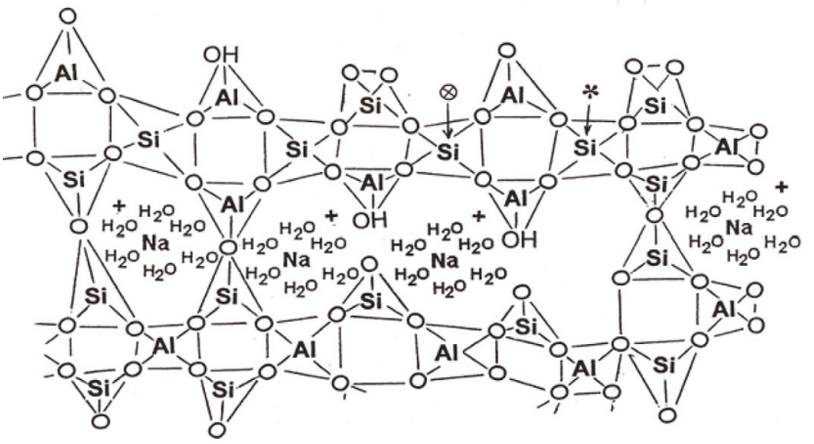


Figure 8.
Barbosa model [35].

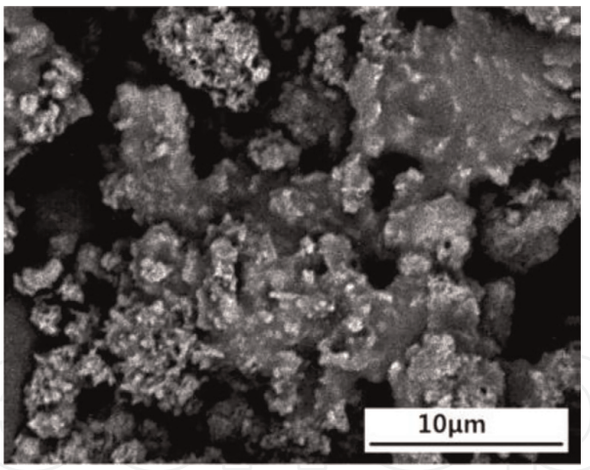


Figure 9.
The SEM micrograph of RM from ACG Plant.

Figure 10 presents the morphological properties of the RHA detected by SEM. It shows a porous and multifaceted particle shape and size. The foremost constituents of rice husk comprise hydrated silica, cellulose and hemi cellulose component and lignin component of approximately. The porous and honeycomb morphology seen can be credited to the burning out of the organic component in the rice husk during combustion.

The XRD diffractogram of RM (**Figure 11**) shows the presence of hematite Fe_2O_3, gibbsite $Al(OH)_3$, $Al_2O_3.H_2O$, lapidocrocte FeO(OH) and calcite $CaCO_3$. RM displays some undisclosed peaks and a few sharp peaks that are mainly from hematite and calcite, but no observable broad humps [36]. This suggests that the amorphous phases are not present at large quantity. By comparison with its chemical composition, alumina mainly presents as amorphous phases. Thus, red mud provides mainly Al (in the form of amorphous Al_2O_3 or dissolved $NaAlO_2$) and NaOH but little Si to geopolymerization.

3.4.2 Microstructure of RM-based GP

There are three parent materials contributing in the synthesis of RHA/RM geopolymers: RM, RHA, and NaOH solution. However, only amorphous phases in raw materials contribute in geopolymerization reaction [36]. Among the three raw materials, the red mud provides NaOH, $A1_2O_3$, and $NaAlO_2$; rice husk ash provides amorphous SiO_2; sodium hydroxide solution provides NaOH.

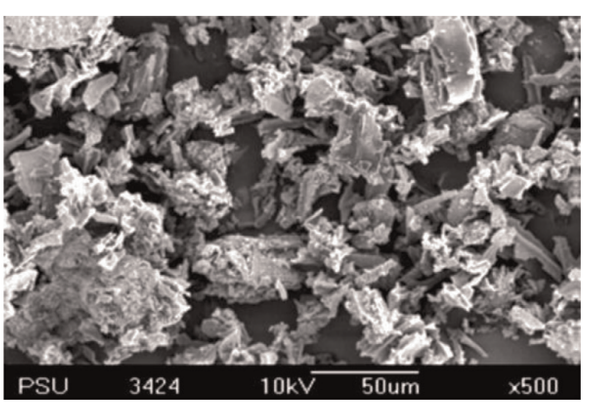


Figure 10.
SEM micrograph of RHA.

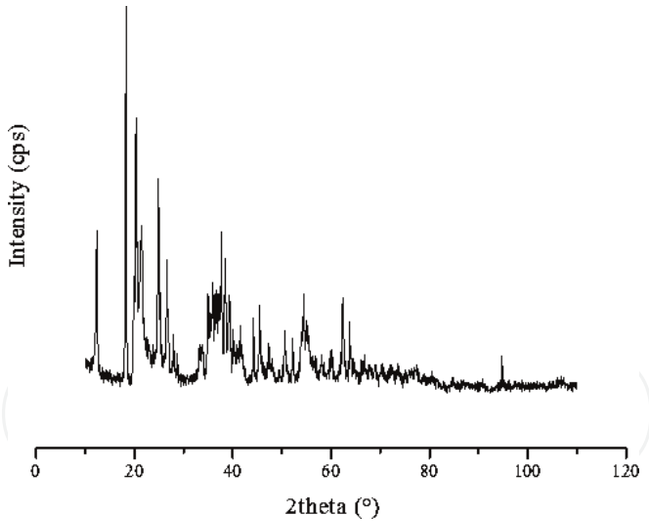


Figure 11.
XRD pattern of red mud.

The SEM [36] of the investigated samples shows that the microstructure of RHA and RM geopolymer comprises non-dissolved particles of RM, which are bonded in an extent gel phase and the formation of gel silicate as shows **Figure 12**. The reaction with the alkaline solution to form a particulate gel network took place at the border of particles then involving the entire surface.

The XRD diagram (**Figure 13**) shows that the product is not clean geopolymer matrix, but a composite consisting of the geopolymer structure and crystalline phases from parent materials. It show a broad reflection related to the high amorphous content. However, the center of this reflection is shifted to $2\Theta = 29°$ due to changes in composition and structure when RHA is activated by NaOH and $NaSiO_2$ solutions. This is in conformity with the microstructure RM and MK-based GP of red mud and metakaolin based-geopolymers comprising undissolved particles of red mud, which are bonded in an extent gel phase [37]. It indicates a Fe content higher than 65% assigned to the existence of undissolved red mud. While, microanalysis of the area presented in **Figure 13** indicated the formation of gel silicate phase (Si > 40% and Fe < 7%). Therefore, red mud may participate within the geopolymeric structures as active and not as reactive material.

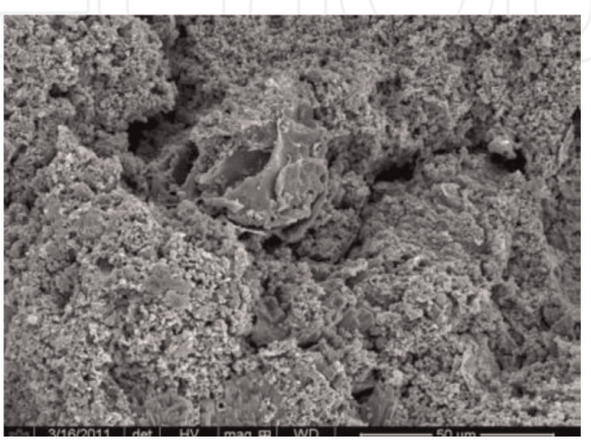


Figure 12.
SEM of RM-RHA based GP [36].

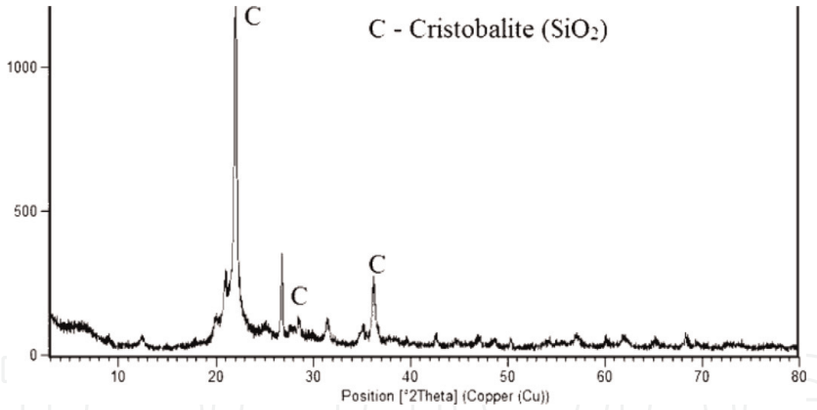


Figure 13.
XRD pattern of RM-RHA based GP [36].

3.5 Mechanical properties

Generally, a strong alkaline medium is necessary to increase the surface hydrolysis of the aluminosilicate [6]. Particles present in the raw material while the concentration of the chemical activator has a pronounced effect on the mechanical properties of the geopolymers; on the compressive strength in particular. Compressive strength is an indication of the compactness and strength of a construction material. Most of the inorganic polymer work reported is consisted upon an extensive discussion of compressive strength and its relation with time, temperature, chemical composition, source material and activating alkaline solutions. Besides compressive strength, flexural strength was also reported in the recent papers. It was observed that aluminosilicate based GP produced higher compressive strength compared to other activating systems. Most of the GPs attained maximum compressive strength within 7 days and only partial increase has been recorded in certain cases. Few papers also reported the descending trend in compressive strength with increasing time. This trend was explained on the formation of crystalline zeolites at extended curing time.

3.5.1 Durability

Geopolymers durability is the most important issue in determining the success of these new materials. The fact that samples that have been exposed to service conditions for in excess of 30 years show little degradation means that geopolymers do therefore appear to stand the test of time [12]. Since those samples were of the (Si + Ca) type conclusion cannot be extended to geopolymers defined as alkali aluminosilicate gel, with aluminum and silicon linked in a tetrahedral gel framework. One of the key unsolved questions in the development and application of alkali activation technology is the issue of durability. Whether geopolymer concretes are durable remains the major obstacle to recognition in standards for structural concrete [33].

Efflorescence is originated by the fact that alkaline and/or soluble silicates that are added during processing cannot be totally consumed during geopolymerization [38]. It is the presence of water that weakens the bond of sodium in the aluminosilicate polymers. In the crystalline zeolites the leaching of sodium is negligible, contrary to what happens in the geopolymers. Na and/or K ions in geopolymers are

bounded only weakly in the nanostructure of the geopolymer gel and are therefore almost completely leachable.

4. Application of geopolymer composites

Several studies have been carried on to produce alkali-activated materials from RM. Due to its low reactivity and low SiO_2/Al_2O_3 molar ratio (<2.0), it has been combined with other higher grade precursors such as metakaolin and fly ash to prepare alkali-activated materials using sodium hydroxide (NaOH) and sodium silicate as alkaline activators solutions. The authors obtained 10.8 MPa compressive strength after 28 days curing. The main application fields of GP are presented in **Table 4**. The potential use of red mud for synthesis of inorganic polymeric composites was studied to use it in the construction sector as artificial structural elements such as massive bricks [9]. RM was reacted with FA, sodium silicate via geopolymerization reaction to get red mud geopolymers which are a viable OPC material that can be used in roadway constructions. Giannopoulou et al. studied the geopolymerization of the red mud and the slag generated in the ferronickel production, in order to develop inorganic polymeric composites with advanced mechanical and physical properties. The inorganic polymeric materials produced by the geopolymerization of the red mud developed compressive strength up to 21 MPa and presented water absorption lower than 3%.

They stated that red mud may be viewed as alternatives in the industrial sectors of construction and building materials [39]. The compressive strength of the RM-RHA geopolymers seems to be enough competitive, which is also comparable to that of all types of OPC with strengths of 9–20.7 MPa. Thus GP can be used as a OPCitious binder to replace OPC in certain civil engineering applications, such as roadway construction, building materials. Moreover, GP-binder has the ability to immobilize toxic chemicals. Potential use of RM in GP synthesis is summarized in **Table 4**. It should be expected that the application of the RM-based geopolymers can bring both environmental and economic advantages [15]. Geopolymerization of the RM and byproducts can save not only the expenses for waste disposal, but also the costs for manufacturing OPC. Then recycling of abundant wastes can minimize

Si/Al Ratio	Application
1	Bricks
	Ceramics
	Fire protection
2	Low CO_2 cement and concrete
	Radioactive and toxic waste encapsulation
3	Fire protection fiber glass composite
	Foundry equipment
	Heat resistant composite 200–1000°C
	Tooling for aeronautics titanium process
>3	Sealants for industry 200–600°C
	Tooling for aeronautics SPF aluminum
20–35	Fire resistant and heat resistant fiber composites

Table 4.
Applications of Geopolymeric materials based on the silica to alumina atomic ratio [9].

their potential damage to the environment. Lastly the elimination of OPC usage can reduce the CO_2 emission caused by firing carbonates.

Silicate-based geopolymer binders have been utilized in applications such as pathways, pavers, mine backfill, railway sleepers, sewerage pipes, and earth retaining [40]. For red mud-based geopolymers to penetrate similar markets, in situ and ambient temperature curing are required. This has been achieved in laboratory trials while targeting a compressive strength above 20 MPa [37].

4.1 Environment considerations on Geopolymers applications

Geopolymer production tackles two main issues of the present time. On one hand, with the increasing amount of waste generation from different processes, there has been a growing interest in the use of waste in producing sustainable building materials to achieve potential benefits. Cleaner production is a pressing issue of our time. Residues or byproducts resulting from different industrial processes requires proper management to ensure a sounder environment [14]. The use of recycled materials in new sustainable materials production is very attractive due to the low-cost related to the waste materials in addition to saving required space for landfill purposes and the development as well as improvement in the materials properties.

On the other, the global warming is one of the most pronounced terms in the present time. Thus reducing the greenhouse gas emissions, which is the main reason behind global warming, is the need of the present time and the future. Efforts are underway to develop environmentally sustainable construction materials, which make minimum utility of fast dwindling natural resources and help to reduce greenhouse gas emissions [41–43]. It is an established fact that the greenhouse gas emissions are reduced by 80% in GP concrete vis-a-vis the conventional OPC manufacturing, as it does not involve carbonate burns. In this connection, GP are showing great potential and several researchers have critically examined the various aspects of their viability as binder system. For manufacturing each tone of the OPC as the primary component of concrete about 1.5 tons of raw materials is needed. Furthermore; in this process about one tone of carbon dioxide will be released into the atmosphere. Geopolymers generate just 0.184 t of CO_2 per ton of binder. Although the CO_2 emissions generated during the production of Na_2O are very high, still the production of alkali-activated binders is associated to a level of carbon dioxide emissions lower than the emissions generated in the production of OPC.

5. Conclusion

In the light of the above it appears clearly that extensive research has been carried out into the field of geopolymers for better understanding the chemical mechanism conducting to their formation and to develop the ability to design geopolymers with specific applications. In particular the variance of source material makes difficult a standard mix design. Nowadays the most investigations agree that source material, mixing ratio, alkali activator, curation time are key factors in the geopolymerization process. With regard to the immense bauxite resources of Guinea, the development of a subsequent alumina industry is expected and implies two questions: (i) a highly qualified manpower is required to manage the very complex issue of the alumina production and the management of the resulting waste; (ii) a worldwide integrated approach will be required to Takle the management of industrial wastes an environmental challenge and a technological opportunity to develop promising engineering application. The valorization of the red mud is at the same ns.

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