PRODUCTION OF PENCIL LEADS FROM ALAWA GRAPHITE BY CONVENTIONAL PRESS AND DRY METHOD

BY

ABUBAKAR Ibrahim Ibrahim

B.Eng (ABU) 2016

P17EGML8006

DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING,
FACULTY OF ENGINEERING,

AHMADU BELLO UNIVERSITY,

ZARIA-NIGERIA

SUPERVISORS:

PROF. I.A MADUGU

DR. AUWAL KASIM

JANUARY, 2022

CHAPTER ONE

INTRODUCTION

1.1Background

Since independence in 1960, Nigeria as a country has been in dire need of sustainable development/growth. The country, no doubt, have witnessed phenomenal economic growth in GDP over the years. It is blessed with so many minerals but not much attention is being paid to the exploration and utilization of these minerals. The major resource that attracts the attention of Nigerians and Nigerian government is crude oil which is depleting fast and its exploitation has adverse effect on environment (Mohammed *et al*., 2014).

Themineral sector alone has the potential to generate abundant wealth with over 5 million employment opportunities if properly harnessed (Lar, 2014). Currently, the mineral sector employs about 450,000 directly and over 2million indirectly. The sectors contribution to GDP averaged 0.37 percent in 2011-2012 to over 12 percent in 2012-2013(Lar,2014) recording a double-digit growth rate; a clear indication that the sector has the capacity to insulate Nigeria from the vagaries of oil shocks and economic uncertainties(Dayi, 2017).

Graphite, a common mineral occurring as soft, lustrous veins in rocks was discovered near Borrowdale in northwestern England in the 16th century. However, because people could not differentiate Graphite and Lead, they referred Graphite as “Black-Lead”. People then cut it into rods or strips, wrapped heavily in twine to provide strength and comfortable handle to the graphite. The finished product was then called “Lead-pencil”. In 1779 scientists discovered that, the material they had previously thought was Lead, was naturally a form of microcrystalline carbon and they named it as Graphite (from Greek “*Graphein*” meaning “to write”).

In the late 18th century, the Borrowdale mine was depleted and as graphite was then less plentiful, other materials had to be mixed with it to create pencils. A French chemist, Nicolas Jacques Conte discovered that; when powdered graphite, powdered clay and water were mixed, molded and baked, the finished product wrote as smoothly as pure graphite. Conte also discovered that a harder or softer writing core could be produced by varying the proportion of clay and graphite. The more the graphite the blacker and softer the pencil lead.

Around 1889, Lother Von Faber, scientist from Germany developed a method of making graphite paste into rods of the same diameter and later invented a machine to cut and groove the pencil wood. Following the depletion of the once-abundant graphite source at Borrowdale, other graphite mines were gradually established around the world.

Graphite, a natural form of carbon,is one of the solid minerals that Nigeria is blessed with andis characterized by its hexagonal crystalline structure. It occurs naturally in metamorphic rocks such as marble, schist and gneiss due to reduction of sedimentary carbon compounds during metamorphism. It also occurs in igneous rocks and in meteorites. When graphite crystallizes in an octahedral system, it becomes diamond. Graphiteisa lustrous black carbon mineral unctuous, and relatively soft with a hardness of 1-2 on the Mohr's scale (Slodkevich, 2009). It is the most abundant form of pure carbon, and exhibits the properties of metals and non-metals making it suitable for many industrial applications. some of these metallic properties include thermal and electrical conductivity while the non-metallic properties consist of inertness, high thermal resistance, lubricity and high melting temperature of about 3,500^oC (Tagiri, 2007).

Graphite, being one of the most important non-metallicMineral finds applications in various industries. More sophisticated applications of graphite are in refractories, expanded graphite-based sealing gaskets, graphitized grease, braid, brushes, brake lining, etc. It is also used in minor amounts as a vital additive for producing foundry coatings to prevent fusion of liquid metal with sand at the mold or core face. Such coatings are either applied by spraying or painting in the form of suspension or by dusting or rubbing as dry powders. Graphite used for coating is of high quality which does not peel off as flakes on drying and imparts a smooth surface to the casting. Graphite, a major additive to many coating systems, is known for its multifarious functions in refractories, lubricants, thermal conductors, electrical conductors, UV shields, electromagnetic pulse shields, corrosion shields and pigments. It is also used as moderator in nuclear reactors. Traditional uses of graphite are found in crucibles, foundries, pencils, etc. (Indian Mineral Review, 2015).

Graphite occurs generally admixed with country rocks and hence, it requires beneficiation in order to obtain desired grade for various end-uses. The Processes for graphite beneficiation dependupon nature and association of the gangue minerals present. The common processes adopted are washing, sorting, tabling, acid leaching and froth flotation. Amongst these, froth flotation process is used widely as it helps in producing a fairly high-grade graphite concentrate. Sometimes, beneficiated concentrate is further enriched by chemical treatment (acid leaching, chlorination, etc.) to obtain a very high-grade concentrate containing 98 to 99% Fixed Carbon (FC) (Indian Mineral Review, 2015).

1.2 Statement of Problem

A lot of works have been done on some Nigerian graphite deposits in an effort to establish their amenabilityto concentration via froth floatation technique. It is however, clear that the majority of these works focused on development of processing routes and characterization of the graphite. However, to the best of my knowledge, no attempt was ever made either by government or individual researchers to utilize theselocalGraphite in production of some graphitic materials such as pencils, battery-electrodes, refractories etc.

Further to this, the process route for the beneficiation of Alawa graphite deposit to pencil grade has been developed and the suitable parameters for floatation of the graphite were established. These parameters were further optimised and the optimum values were found to be; 50µm, 2ml, 2ml, 3ml, and 8.5 particle size, collector, frother, depressant volume and pH value respectively (Akindele *et al*., 2019). The present research aims to take advantage of these findings to further concentrate thegraphite and produce pencil leads.

Moreover, despite the fact that the Country is blessed with abundant graphite deposit, yet the Government is still spending seven hundred and fifty billion naira annually to import pencils (Idongesit, 2017).

1.3 Justification/Significance of the Study

Considering the fact that Nigeria is blessed with abundant graphite deposits and sources for other pencil production ingredients, with the view that pencil production requires less sophisticated technology, the Federal Government in the early 2016 made a projection on the commencement of pencil production in the year 2018, which is capable of creating about 400,000 jobs across the country. PRODA (the Project Development Agency) conducted a holistic research on pencil production which gave an insight on the feasibility of the entire project. Currently, the Federal Government has commenced the installation of equipment and machines for the proposed pencil production factory at the Project Development Institute (PRODA), Enugu. Hence, the findings from this research if implemented, will:

i. create further awareness on the potential of Alawa graphite deposit for use in pencil making, which will enable prospective investors and government to venture into the business.
ii. create job opportunities and provide additional source of revenue to the people and/or government, by attracting local and foreign investors.
iii. bring to fore the potential of Alawa deposit as a source of raw materials for pencil production in Nigeria.

1.4 Aim and Objectives

The aim of this study is to producePencil Leads from Alawa Graphite by conventional Press and Dry method

The objectives of the study are to:

i. concentrate Alawa graphite deposit by froth flotation technique;
ii. design and developan extrusion die for pencil leads production;
iii. produce pencil leads and case using conventional press and dry method;
iv. assess the integrity of the developed pencil.

1.5 Scope of the Study

This research involves sourcing the Alawa graphite, concentration of the graphite deposit sample to pencil grade using froth floatation technique, construction of pencil-leads extrusion die and eventually using the processed sample and constructed extrusion die to produce pencil leads.

CHAPTER TWO

LITERATURE REVIEW

2.1 Graphite

Graphite is a very versatile industrial mineral with unique properties that have facilitated technological innovation, beginning in the 16th century with the discovery of high-grade lump graphite at Borrowdale, England. The Borrowdale graphite was carved into pencil sticks for convenient durable markers and had strategic importance as a refractory lining in moulds that produced superior, smooth and round cannonballs with greater projectile range. Today natural graphite is a key component in high-performance refractory linings for steel manufacture, high charge capacity for lithium-ion batteries, and a source of graphene to inspire a new generation of smart materials (Keeling, 2017).

Graphite is a naturally occurring crystalline form of carbon. It is a native element mineral found in metamorphic and igneous rocks. It is extremely soft, cleaves with a very light pressure and has a very low specific gravity. In contrast, it is extremely resistant to heat and nearly inert in contact with almost any other material. These extreme properties give it a wide range of applications in metallurgy andother industries (Taylor, 2005).

2.1.1 Structure and characteristics of Graphite

Generally,Graphite consists of rings of six carbon atoms and the sp^2 carbon atom of the hexagonal basal plane has three σ electrons in the same plane and one π electron in the perpendicular direction, giving it a bond strength of 524 kJ/mol. A weak Van der Waals forces of about 7kJ/mol exist between basal planes(Dobbet al.,1995). The rhombohedral crystalline structure having an ABCABC stacking sequence accounts for up to 30% of the structure in the natural graphite, but is converted to a hexagonal structure at temperature higher than 1300^{o}C due to the former's low stability compared to hexagonal graphite(Wilhelm *et al*., 2007). Figure 2.1: is an illustration of the crystal lattice of a hexagonal graphitewith an ABAB stacking sequence(Terrones *et al*., 2010).

Graphite has low thermal expansion, outstanding thermal shock resistance under rapid changes in temperature and good chemical stability(Sang-Ming *etal*.,2015). Other advantages of graphite include; electrical and thermal conductivity, dewatering, and self-lubricating. It is widely used in nuclear reactors because of its high temperature strength and high tolerance to neutron irradiation compared to other metals and ceramics(Xiaowei *et al*., 2004).

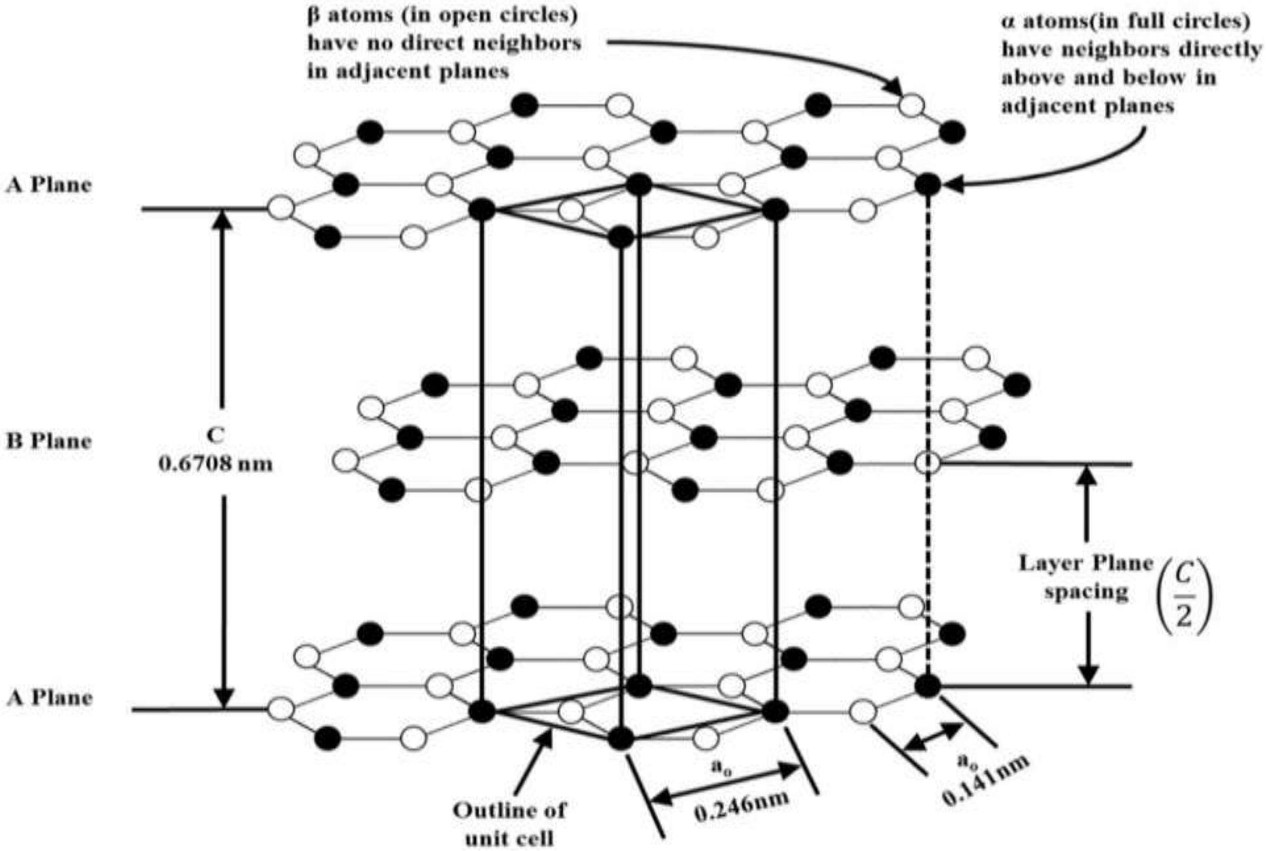


Figure2.1:Crystal structure of graphite showing ABAB stacking sequence and unit(Inagaki,2001)

2.2 Geological Occurrence of Graphite

Carbon is the fourth most abundant element in the solar system, and in terms of its abundance in Earth's crust, is ranked about 12th to 17th in abundance with an estimated crustal concentration between 180 and 270 parts per million. The abundance of carbon in Earth's crust is difficult to determine because carbon stores exist and cycle between rock, sediment, atmosphere, biosphere, and ocean reservoirs. The behavior of carbon in its geochemical cycle is influenced by the form in which the carbon occurs. Most of the carbon in the Earth's crust (approximately 80-90%) is contained in carbonates minerals and in carbonates rocks. Most of the remaining carbon in the Earth system occurs in living and Fossils organic matter and as carbon dioxide in the atmosphere or dissolved in the Ocean. These remaining carbon forms, dominate the carbon cycle. Graphite makes up only a small proportion of the carbon in the Earth's crust, probably less than 0.5%, and much of this graphite is formed byhigh-temperature thermal alteration of organic matter from biogenic sources deposited in sedimentary rocks and subsurface reservoirs. The mineral graphite is stable and inert in the crustal environment and is unchanged under surface weathering conditions. Burial and thermal metamorphism tends only to recrystallize graphite. Therefore, graphite is largely isolated from the overall carbon cycle (USGS, 2017).

Generally, graphite is formed when carbon is subjected to heat and pressure in the earth's crust and in the upper mantle. A pressure of about517106.797kPa and a temperatureof 750°Care needed to produce graphite. This results to granulite metamorphic facies(King, 2005).

2.3 Sources of Graphite

Commercial sources of natural graphite are commonly classified as; flake graphite, vein or lump graphite, and amorphous(microcrystalline)graphite. These reflect the geological setting and condition under which the graphite is formed. Table 2.1 is a summary of characteristics of different forms of commercial natural graphite.

Table 2.1: Summary of characteristics of different forms of commercial natural graphite

	Flake	Vein	Amorphous
Description	Crystalline-graphite flakes; coarse>150µm; fine<150µm	Interlocking aggregates of coarse graphite crystals; typically>4cm	Microcrystalline, soft earthy graphite; mostly<40µm
Origin	Syngenetic; regional Metamorphism of organic matter in metasedimentary rocks	Epigenetic regional metamorphism; metasomatism involving CO_2-CH_4-H_2o fluids	Syngenetic; contact and/or regional thermal metamorphism of coal seams
Ore	2-30% graphite; strata-bound, tabular or lenses	>90% graphite; veins and fracture infill	>70% grahite; in anthracticitic coal layers, typically folded and faulted
Product grade	85-97% Cg	90-99% Cg	75-90% Cg
Main uses	Refractories, batteries, brake linings, flame retardants	Carbon brushes, brake linings,batteries, lubricants	Steel recarburizers, foundry mould facing, lubricants, pencils
Major producers	China, Brazil, India, Canada	Sri Lanka	China, Mexico, North Korea Turkey.

(*Source*: Mitchell ,1993)

2.3.1 Flake Graphite

This is associated mostly with high grade metamorphic rocks where organic carbon deposited within sediments was transformed into graphite at a pressureabove 500 MPa and temperature above 700^{o}C.The process of metamorphic graphitization is controlled largely by temperature and essentially complete above 500^{0}C (Wang 1989). Pressure, duration of the metamorphic event, increasing temperature and shear strain influence the degree of crystallization and the size of graphite flakes(Beyssac et al., 2002). Plate I is a micrograph of coarse flake Graphite

PlateI: Coarse flake graphite (>300 µm) (Keeling, 2017)

2.3.2 Vein Graphite

Vein graphite occurs naturally as vein, fracture fill or pipe-like bodies when graphitic carbon and/or carbon-rich fluids (pegmatites i.e high temperature fluids which is formed regionally or locally when a mass of magma cools) migrated and precipitated as graphite masses. High-grade, vein-style graphite is found from several countries, but at present, it is produced in commercial quantities only from Sri Lanka, a long-term supplier. Former sources include the historic Borrow-dale mine where highly crystalline graphite forms pipe-like bodies, fracture fill and disseminated replacements.Recent studies concluded that these are formed as the result of dehydration and rehydration reactions of CO_2 and CH_4 fluids, generated during dioritic magma assimilation of organic-rich metapelites at comparatively low temperature and pressure of 400–500 °C and 100–200 Pa, respectively(Luque *et al*., 2009). Vein graphite from Sri Lanka shows needle-like macro morphology and flake-like micro morphology and is produced as centimeter-sized lumps of mostly high purity graphite (94–99% C) (Keeling, 2017).

Plate II: Lump Graphite (*Source*: Geology.com)

2.3.3 Amorphous Graphite

Amorphous graphite is produced mostly from anthracitic coal seams that have undergone variable graphitization during contact or regional metamorphism. This form of graphite is typically massive and has comparatively high levels of fine-grained impurities that are not easily separable from the graphite. Commercial grades typically range from 75 to 85% C. Some amorphous Graphite are also produced as a fine-grained Graphite byproduct from flake graphite mining and processing (Keeling, 2017).

Plate III: Amorphous Graphite (*Source*: Geology.com)

The total production of natural graphite in 2019 was estimated to be 1.1 Mt with China the largest producer as shown in Figure 2.3. Natural graphite produced was comprised of 40% amorphous graphite – predominantly from China and Mexico; 60% flake graphite – dominated by China with significant production also from India and Brazil; and <1% vein graphite from Sri Lanka. North America produced only 4% of the world’s graphite supply with production in Canada and Mexico. No production of natural graphite was reported in the United States, but two companies were developing graphite projects-one in Alabama and one in Alaska (United States Geological Survey, 2020).

Large deposits were being developed in Madagascar, northern Mozambique, Namibia, and South-central Tanzania. Some mines in Madagascar began ramping up production in 2018, and a mine in Tanzania started sampling production in the beginning of 2017. A graphite mine project in Mozambique commenced operations at the start of 2018 and was ramping up production during 2018 and 2019 at a high-grade graphite deposit, which was reportedly the largest natural graphite mine globally. The mine cut back production during 2019 in an effort to stabilize graphite prices. The mine is expected to operate for 50 years (USGS, 2020).

Table 2.2:Natural graphite production by country in 2019. (Source: USGS, 2020).

Country	**Mines Production**		**Reserves**
	2018	**2019**	
United States	---	---	(3)
Australia	1,000	1,000	(3)
Brazil	95,000	96,000	72,000,000
Canada	40,000	40,000	(3)
China	693,000	700,000	73,000,000
Germany	800 800		(3)
India	35,00035,000		8,000,000
North Korea	6,000	6,000	2,000,000
Madagascar	46,90047,000		1,600,000
Mexico	9,000	9,000	3,100,000
Mozambique	104,000	100,000	25,000,000
Namibia	3,460	3,500	(3)
Norway	16,000	16,000	600,000
Pakistan	14,000	14,000	(3)
Russia	25,200	25,000	(3)
Sri Lanka	4,000	4,000	(3)
Tanzania	150	150	18,000,000
Turkey	2,000	2,000	90,000,000
Ukraine	20,000	20,000	(3)
Vietnam	5,000	5,000	7,600,000
Zimbabwe	2,000	2,000	(3)
Others	200200		(3)
World total rounded	**1,120,000**	**1,100,000**	**300,000,000**

(*Source*:USGS,2020)

2.4 Synthetic Graphite

Synthetic graphite is made by heating amorphous carbon materials, such as calcined petroleum coke, coal or natural and synthetic organic materialsin a reducing environment at temperatures between 2,300 to 3,000 °C. The process of preparation, heating and cooling takes several weeks to several months. Graphite fibres are manufactured by high-temperature conversion of polyacrylonitrile, pitch or rayon precursors (Keeling, 2017).

2.5 Graphite and Diamond

Graphite and diamond are the two mineral forms of carbon. Diamond forms in the mantle under extreme heat and pressure. Most graphite found near Earth's surface was formed within the crust at lower temperatures and pressures. Graphite and diamond share the same composition but have different structures. The carbon atoms in graphite are linked in a hexagonal network which forms sheets that are one atom thick. These sheets are poorly connected and easily cleave or slide over one another if subjected to a small amount of force. This gives graphite its very low hardness, perfect cleavage, and slippery feelcontrary to Diamond (Hugh, 2009).

2.6Synthetic Vs Natural Graphite

Figure 2.4 shows Synthetic and natural graphite supply, separate markets with increasing overlap in their uses. Price and purity are the two most important factors behind the market separations.Synthetic graphite is engineered to known specifications with high purity and predictable properties, but is less conductive and more expensive than natural graphite. Synthetic graphite is used to make electrodes for metal refining, principally in electric arc furnaces used for steel production and large cathodes that line electrolytic cells used in Aluminum smelting. Other uses include graphite blocks and powders, carbon brushes and bearings, and graphite fibrereinforcement in polymer composites. Natural amorphous graphite is used as a carbon raiser in iron casting and steelmaking, as a facing on foundry moulds, and for pencil manufacture. Flake graphite is consumed mainly in the productionof high-performance refractories. These are used in steelmaking to line ladles and the zones most vulnerable to corrosion due to slag in basic oxygen and electric arc furnaces,usually in the form of magnesia-carbon bricks or alumina-graphite casting ware and monolithic refractories (Ewais 2004; Stein and Aneziris 2014). Coarser grades of flake graphite have a slower rate of oxidationand are preferred by refractory manufacturers, but surface treatments and antioxidants are widely used that also improve the performance of more readily available medium-flake graphite (Ewais 2004; Lee and Zhang 2004).

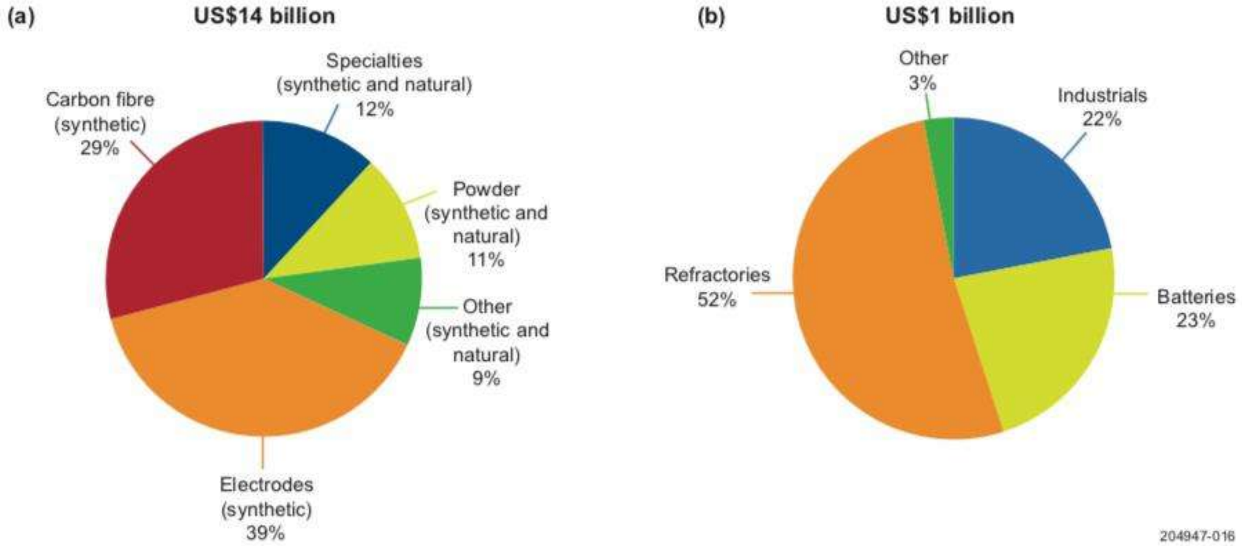


Figure 2.3: Global Graphite markets by value in 2012. (a) Synthetic and natural Graphite. (b) Natural flake Graphite excluding amorphous Graphite. (Source: Roskill, 2015; AMG Graphite, 2015; SGL Group, 2014).

2.7 Graphite Demand

Synthetic graphite makes up over 90% of the global graphitic carbon market, which was estimated during peak demand in 2012 at around $US14 billion, as shown previously inFigure 2.4. Independent estimates of natural graphite demand for 2014 and 2015 were <700,000 tpa as shown inFigure 2.5, with significant oversupply driving lower prices (Schodde 2016; Spencer and Hill 2016). Demand for flake graphite wasunder 400,000 tpa, but was anticipated to rise substantially in line with the growth in manufacture of lithium-ion batteries for portable devices, electric vehicles and energy storage as shown in Figure 2.5.Natural graphite accounted for less than 10% by value but the quantities produced were the same with ~1.2 Mt natural graphite and ~1.5 Mt synthetic Graphit.

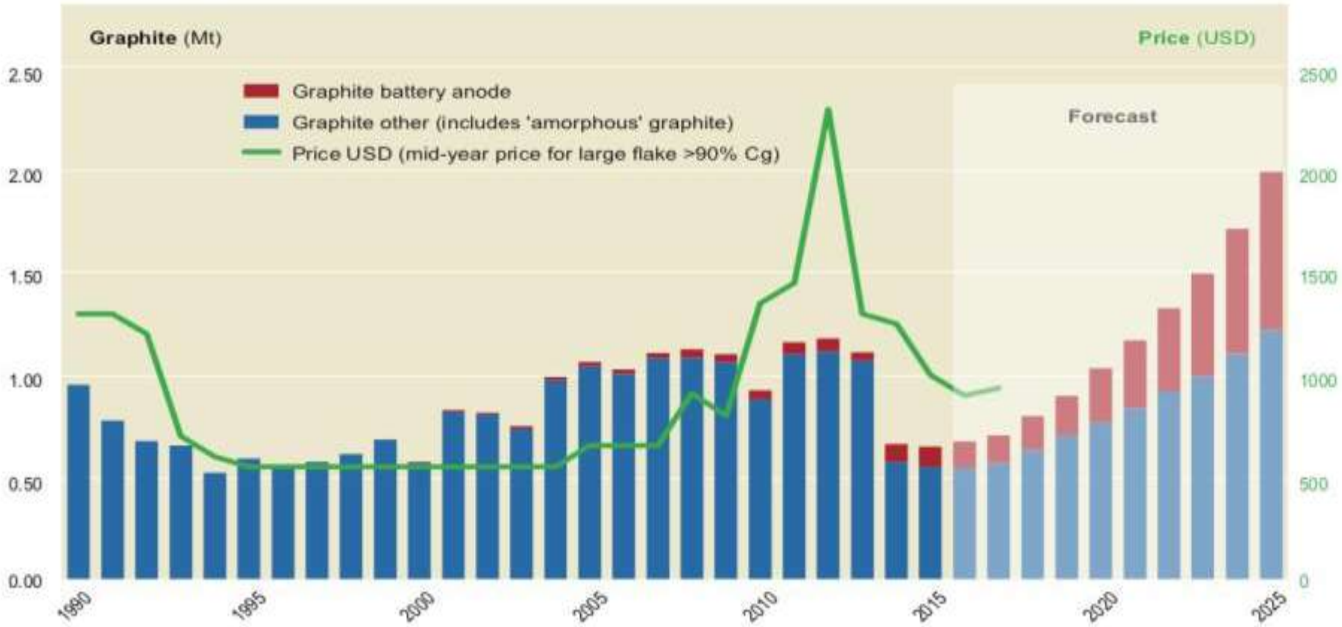


Figure2.4:Historical and forecast demand for natural graphite (1990–2025) with graphite for battery anode highlighted in red; historical price trend for natural graphite, large flake >90% Cg shown in green. (Sources: Roskill, 2015;Spencer and Hill, 2016; Schodde, 2016).

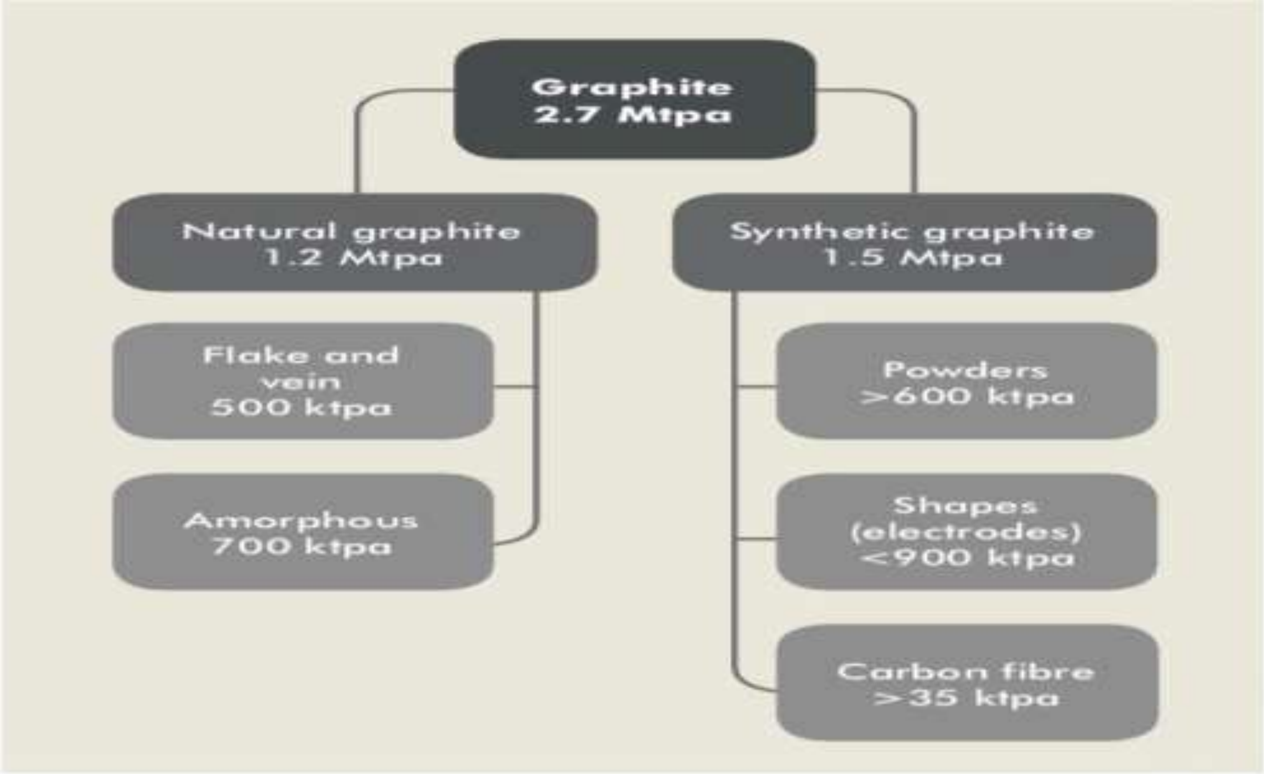


Figure 2.5: Global graphite production by estimated tonnage in 2012. (Sources: Roskill, 2015; AMG Graphite, 2015; SGL Group, 2014)

2.8 Graphite Occurrence in Nigeria

Geological Survey of Nigeria (GSN, 1973) reported some occurrences of Graphite deposits. These deposits occur in Birnin Gwari of Kaduna State, Gayama area of Taraba State, Maiyo Butale, Hossere Nuwa and Jauro Jalo area of Adamawa State, and in Duchin Hai (Dutsen Haiyar) in Bauchi State. Graphite deposit is also found in Alawa area of Niger State.

i) Birnin Gwari graphite in Kaduna State

Russ (1957) and Truswell and Cope (1963) described a number of Carbonaceous Schist occurrences within the Kushaka Schist formation which comprises predominantly semi-peitic meta sediments but with some psammites, pelites and amphibolites. The Kushaka Schist formation forms a belt, 40 to 50 km wide, trending N-S along the eastern border of sheet 31. It can be traced further to the north and south for a total length of 260km (GSN, 1974). The carbonaceous Schist is predominantly composed of Quartz Biotite and Muscovite and some contain Garnets (Truswell and Cope, 1963). The graphite occurs in small amounts though few assays are available, e.g. 2.78% carbon at Iburu (Russ, 1957) and 4.37% carbon some 6.5 km north of Birnin-Gwari (old town), 90 km NW of Kaduna. This deposit is powdered and fine-grained.

ii) Graphite deposits in Adamawa State.

In 1957, Geological Survey of Nigeria reported occurrence of graphite in Adamawa. Unfortunately, no records are available concerning Hossere Nuwa, and Jauro Jalo occurrence but that of Maiyo Butale (08000’20” N and 110 59’ E) have been examined. The deposits at Hossere Nuwa (070 51’ N and 110 24’ 30” E) and Jauro Jalo (070 37’30” N and 110 08’ E) have not been examined. They occur in areas of migmatites (Ikejiaku, GSN field map, sheet 256) and Jauro Jalo is in mountainous country along a major geomorphological feature (more than 30 km long) trending N600W.

iii) Gayama graphite in Taraba State

In 1957Geological Survey of Nigeria reported the occurrence of graphite in Gayama Area of Taraba State. Its occurrence is found at Gayama (07^{o}47’N and 11^{o}10’30’’E).

iv) Duchin Hai (Dutsen Haiyar) graphite in Bauchi State

Falconer and Raeburn (1923)first reported this locally and was laterexamined in more detail and described by Jacques (1943). The deposit occursat approximately 11008’ N and 90 41’ E on the west bank of the Delimi, (Bonga) River inNingi L.G.A., and due ENE of Ningi town which is about 90 km North-West of Bauchi.Presently, an old pit of 24 m long, 3.5 m wide and 2 m deep which is partially filledwith debris exist. There are also three additional trenches dug to the north and south ofthe old pit. The graphite occurs in a schistose band striking N100W, dipping 600 to 800eastward and can be followed for about 80 m along strike. Towards the north end, thegraphite quartz-Ferruginous band narrows to less than 1m and is more ferruginous, whileto the south it widens to 4 m or more and contains higher graphite content up to 30%.This graphite is known to occur as flakes between quartz crystals.

2.9 Uses of Natural Graphite

Natural graphite is mostly utilized in making refractories, batteries, pencils, carbon raiser during steelmaking, pencil, expanded graphite, brake linings, foundry facings and lubricants. Graphene, which occurs naturally in graphite, has unique physical properties and is among the strongest substances known; however, the process of separating it from graphite requires more advanced technology (USGS, 2009).

2.9.1 Pencils

From the 16th Century, pencils were made with leads of English natural graphite, but modern pencil lead is most commonly a mix of powdered graphite and clay; it was invented by Nicolas-Jacques Conté in 1795 (Ritter, 2001). It is chemically unrelated to the metal lead, whose ores had a similar appearance, hence the continuation of the name. “Plumbago” is another older term for natural graphite used for drawing, typically as a lump of the mineral without a wood casing. The term plumbago drawing is normally restricted to 17th and 18th century works, mostly portraits.

The ability to leave marks on paper and other objects gave graphite its name, given in 1789 by German Mineralogist Abraham Gottlob Werner. It stems from graphein, meaning to write/draw in Ancient Greek (Delhaes, 2001). Today, pencils are still a small but significant market for natural graphite. Around 7% of the 1.1 million toneof Graphite produced in 2011 was used to make pencils (Anon, 2017).

Generally, pencils create marks by physical abrasion, leaving a trail of solid core material(graphite) that adheres to a sheet of paper or other surfaces. They are distinct from pens, which dispense liquid or gel ink onto the marked surface(Petroski, 2010).

2.9.2 Battery Anodes

Both synthetic and natural graphite make effective, stable anodes for batteries. Increased demand for graphite in this market is being driven by the growth in manufacture of lithium-ion batteries. High electrical storage and good charge cycling characteristics can be achieved using natural graphite after treatment by impact milling to crumple the flakes into spherical shapes as depicted in figure 2.8, followed by acid or thermal purification (>99.5% C), then coating with a thin film of amorphous carbon (Yoshio et al., 2004).

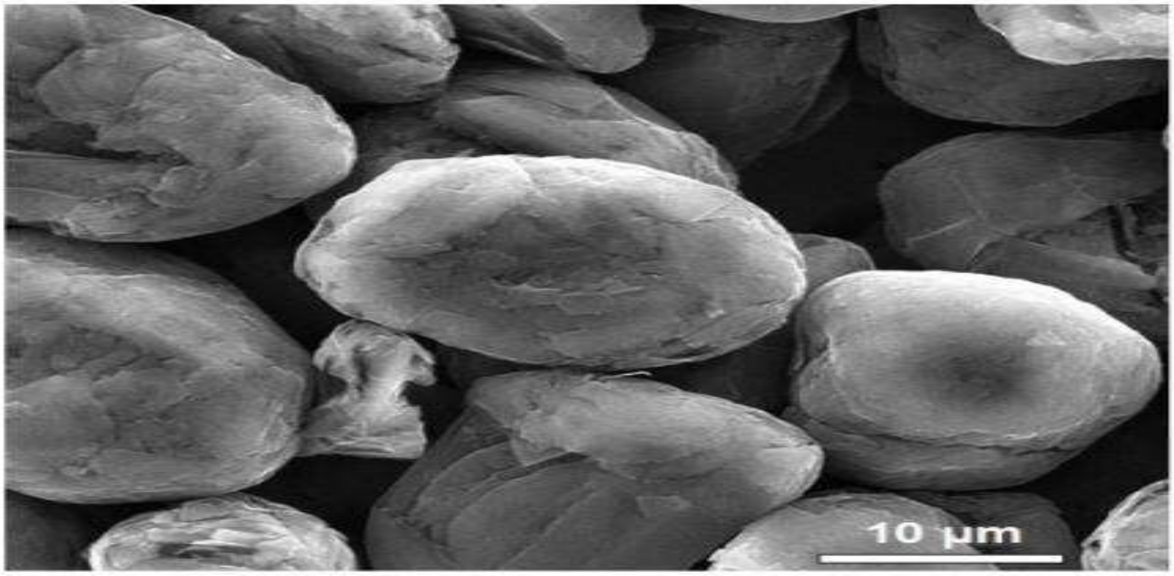


Plate Ⅳ: Spherical Graphite shapes for battery anodes produced by milling flake graphite.
(*Source*: Keeling, 2017)

2.9.3 Expandable Flake Graphite

Demand for expandable natural flake graphite is also expected to increase, principally for use as a fire-retardant additive in foam, plastic and various construction materials (Ghilotti, 2016). For this use, suitable flake graphite is intercalated with chemical species (e.g. Halogens, Sulfate, Nitrate, Organic Acids, Ferric Chloride) which will rapidly gasify at high temperatures causing the graphite to exfoliate/expand to between 80 and 300 times. Coarse flakes (>300 µm) has the highest expansion but finer sizes (<150 µm) are preferred for some applications. On expansion, graphite retards the spread of fire and minimizes the creation of toxic gases and fumes. Expanded graphite can also be interlocked and compressed to give an essentially flat, flexible, integrated graphite foil, which is widely used as gaskets and seals, with potential use also as a separation layer in fuel cells and redox flow batteries (Chung, 1987).

2.10 Clay and its Compositions

Clay is an earth material that is plastic when moist but hard when fired, and composed mainly offine particles of hydrous aluminumsilicatesandother minerals (Rao, 2013). Based on composition it is defined as crystallized aluminum silicate associated with other impurities. Secondary components of clay can be quartz grains and, more rarely, zircon, apatite, granite and others (Saba, *et al*.,2014). Clays oftencontainadmixtures as iron hydroxides.Also clays can contain anorganic substance.

2.11 Classification of Clay based on Mineralogical compositions

Based on its mineralogical compositions, Clay can be classified into four: Kaolinite($Al_4(OH)_8Si_4O_{10}$),Montmorillonite (complex hydratedsilicates of Al,Mg andNa),illite(complexhydratedsilicatesofAl,Mg,Fe, and Na)andHaloizite

($Al_4(OH)_8Si_4O_{10}\times4H_2O$) as wellas around 30differenttypesofpureclayswithinthesecategories (Uddin, 2008).One subgroup of the Montmorillonite is Bentonite clay.Duetotheir useful propertiessuch as high capillarity,unique rheological properties, hardening, plasticity,thixotropy,high degree of swelling as well as high degree of efficiency for M^+ cation exchange (Parvinzadeh, *et al*., 2010).Today clayshave an important role in modern industries. The high capillary and porosity of clay enables the absorption of large amounts of water. Thethixotropyis propertyof some clays when kneaded they become more viscous. Kneading also increases the shaping ability that is a consequence of a change in the electrical nature of clay surfacelayers. Swelling is a very important feature ofclaymineralsthatenables their wideapplicationinvariousindustriesin the field of geotechnicalengineering,environmentalengineeringand other industrialapplications.Highdegreeof efficiency for M^+ cation exchange is the result ofcharge imbalances in clay structure caused by exchange of Al^{3+} for Si^{4+} in the tetrahedral sheets, and of Mg^{2+} for Al^{3+} cations in the octahedral sheets.

2.12 Types of industrial Clays

Clays have been used by Man since pre-historic times. Initially they were used almost entirely in the fabrication of ceramics, nowadaysthey find numerous industrial and technological applications. Industrially, they are used in the production of materials with large added value such as nanocomposites,cosmetics, pharmaceuticals etc. They are also used in production of pencils(coloredand black-lead). Christidis, (2011) established that there arefourtypesof industrial clays, namely:

i. Bentonite
ii. Kaoline

iii. Fibrous clays(Palygorskite and Sepiolite)
iv. Common clays and shales

2.13.1 Bentonite

Bentonite is a colloidal aluminum-silicate clayformed by alteration of volcanic material (Bergaya & Lagaly, 2000; Grim & Guyen, 1978). It consists of several minerals out of which the dominant one is montmorillonite that makes at least 70% of its composition (Abdou and Ahmed, 2011). Bentonite, in addition to montmorillonite, contains asmall portion of other mineral matter, usually quartz, feldspar, volcanic glass, organic matter, gypsum, or pyrite whose total share in bentonite is about 30% (Gates *et al*., 2002). There are different types of Bentonitebasedon the dominant chemical element such as Potassium, Sodium, Calcium,and Aluminum.From industrial applications point of view, the most common are the Sodium and Calcium Bentonites. These are three-layer Alumino-silicate clays with an ability to swell and increase volume when in contact with water. Sodium bentonite shows higher swelling capacity compared to the calcium bentonite because the sodium cations may be hydrolyzed to a greater extent than the calcium cations(*Gleason et al*.,1997). Thisfeature provides bentonite an excellent cohesiveness and makes it an excellent bonding and sealing material.

2.13.2 Kaolin (China Clay)

Kaolin (China Clay) is chemically inert and can be prepared as a white powder specified according to its whiteness and brightness. It is ideal for a wide range of ceramic, filling and coating applications, where the appearance of the finished product is important (Jepson, 1984). It is particularly valuable as a surface coating pigment on high quality glossy paper, which might contain up to 30% of the mineral.

2.13.3 Fibrous clays (Palygorskite and Sepiolite)

Sepiolite and Palygorskite are natural micro-fibrous clay minerals whosestructural, morphological and textural features are useful in preparation ofwide variety of advanced nanostructured materials, essentially regarding their ability to render nanocomposite materials. The silanol groups located on the external surface of these silicates and their surface electrical charge are the centers for interactions with biopolymers, such as polysaccharides, proteins, lipids andnucleicacids.

2.14 General Properties of clays

The following subsequent sub-sections discuss the general properties of Clays

2.14.1 Particle size and shape

The size and shape of clay minerals’ particles and aggregate characteristics affect the physical properties of industrial clays. Clay minerals are in principle 2 mm in size. Nevertheless, minerals of the kaolin group often form larger crystals,which in the case of dickite, may reach up to 20 mm althoughdisordered minerals of the group are considerably2 mm (Beaufort et al., 1998).Smectites tend to formsmaller crystals and the average smectite crystal size in bentonites is 0.5 mm (Grim& Guven, 1978; Christidis, 1995). Smectites exceeding 2 mm in size are uncommon.Palygorskite and sepiolite form fibres which often exceed 2 mm in size and have striations (Martin Vivaldi & Robertson, 1971; Jones & Gala´n, 1988).The small crystal size yields a large specific surface area for most clay minerals. This is especially true for smectite, vermiculite,sepiolite and Palygorskite, which have large fractions of internal surface area.

2.14.2 Ion-exchange properties

Cation exchange capacity is a characteristic property of all clay minerals and is of particular importance for smectites and vermiculites and to a lesser degree of sepiolite andPalygorskite. Itis normally measured at pH of 7. It is related to substitutions inthe tetrahedral and/or the octahedral sheet which create a charge deficit known aslayer charge and to adsorption or dissociation of protons at crystal edges often referredto as interrupted bonds at the edges of the crystals. The charge which results from structural substitutions is the ‘permanent charge’. The charge from interrupted bondsbetween the structural cations and the oxygens or the OH groups of the tetrahedraland the octahedral sheet at the edges of the crystals is known as the non-permanentor pH-dependent charge. The layer charge is balanced by the interlayer cations (Na,Ca, K, Mg, H and Li), which are exchangeable. The role of non-permanent charge ismore important for kaolinite than for smectite and vermiculite because of the limitededge surface of the latter.

2.14.3 Hydration and Swelling

Clay minerals tend to adsorb water molecules on their external surfaces, mainly in interrupted bonds or in their interlayer spaces, associated with the interlayer cations or with the internal surface. Gu¨ven (1992a) reported that; with increasing water activity, the following modes of clay hydration are distinguished: (1) ‘interlamellar hydration’ via adsorption of limited amounts of water molecules on the internal surfaces of clay particles; (2) ‘continuous (osmotic) hydration’ via unlimited adsorption of water on the internal and external surfaces of clay particles; and (3) capillary condensationof free water molecules in the interaggregate and intraaggregate micropores. Interlamellar hydration affects mainly smectite and vermiculite and depends:(a) on the hydration energy of the interlayer cations and the polarization energy of the water molecules by the interlayer cations; (b) on the variation of electrostatic potential on the clay surface determined by the magnitude and distribution of the layer charge on the silicate layers; (c) on the activity of water; and (d) the size and morphology of clay particles and the clay fabric (McEwan & Wilson 1984; Guven, 1992a). At low water activity, interlamellar hydration is controlled by the interactions of the interlayer cation with the water molecules forming water complexes and to a lesser degree by interactions of the water molecules with the clay surface. Interlamellar hydration leads to interlamellar or crystalline swelling and may lead to intercalation of 0 to 4 discrete layers of watermolecules between individual 2:1layers (Laird, 2006).

2.14.4 Color Properties

Colour is an important property of clays which are utilized as fillers such as Kaoline and white bentonites (Christidis & Scott, 1997; Pruett & Pickering, 2006; Murray, 2007). In most applications, fillers have to be white. Colour is affected by differences in particle size and shape and by mineralogical and chemical characteristics; in general, the finer the particle size, the whiter the colour (Grimshaw, 1971; Scott, 1990a; Christidis & Scott, 1997; Christidis et al., 2004). The sensation of colour results from stimulus which is transferred from the retina via the optic nerve to the brain (Billmeier & Saltzman, 1981). The human eye responds to wavelengths in the visible spectrum (from 400 nm for the violet to 700 nm for the red colour). Colour can be described from its three attributes, namely hue (the dominant colour which corresponds to a wave length), the saturation known also as purity or chroma (the density of colour) and the brightness known also as lightness or value or whiteness (the light intensity or visual lightness of a colour).

2.14.5 Plasticity

Plasticity is the property of a material to be deformed under stress and to retain the new shape after the stress is removed. It is a characteristic property of clays because other minerals which may be of clay size are not plastic. The nature of plasticity is related to the water molecules which are adsorbed on the clay mineral surfaces forming a rigid film with certain order, which links together clay particles (Grimshaw, 1971). The clay particles form coherent networks, which can deform and retain their shapes after the stress is removed. If the clay aggregates form band-like textures, the network can be deformed by rotation of particles (Lagaly, 2006). Alternatively, if the particles form card-like textures (i.ethe particles are linked with an edge-to-face mode forming T-type contacts) they can be shifted without loosing their coherency, provided that the water content does not exceed a certain limit (Lagaly, 2006).

The plasticity of clays is affected by the type of clay mineral, the amount of water present, the particle size, shape and size distribution of clay aggregates, the specific surface area of the clay particles, the orientation of particles in the aggregates, the nature of non-clay minerals and the previous history of the clay (Grimshaw, 1971).

2.14.6 Rheological properties

The science of the deformation and flow of matter is known as ‘rheology’ (Hiemenz & Rajagopalan, 1997). The viscosity of a liquid is a measure of the internal resistance offered to the relative motion of different parts of a liquid. Clay suspensions can display Newtonian, Bingham plastic, shear thickening (pseudoplastic) or shear thinning (dilatant) behaviour and may develop yield stress (Lyckham & Rossi, 1999). Clays are often used in suspensions. Suspensions of Kaolines are used in the slip casting processes during the manufacture of ceramics and in coating paper, whereas Smectite and Attapulgite are used in drilling fluids. In these applications, the flow properties of the suspensions are of primary importance.

2.14.7 Organic reactions

Clays are known to interact with various organic compounds to form various complexes, via several types of chemical bonds between the oxygen surfaces and the organic molecules (Mortland, 1970). This reaction, which converts clay surfaces from hydrophilic to hydrophobic, yields organoclays (Lagaly *et al*., 2006; de Paiva *et al*., 2008). The intercalation of certain organic molecules is used in the identification of clay.

2.15 Applications of Clays

The easy availability of clays in almost all inhabitable places on earth and its certain characteristic properties facilitate its diverse use in the human civilisation since prehistoric time. Clays were widely used in building muddy huts or in the production of bricks, potteries etc. even in the most primitive forms of cultures. In the present age, the uses of clays and clay minerals are increasing day by day, and they are gradually replacing metals in various fields as cheaper, better and environment-friendly alternatives (Mukherjee, 2013). Clays are used in the following industries:

i. because of their excellent colloidal and rheological properties, clays are used as lubricants in Oil and Gas and drilling industries.
ii. the possibility of swelling allows clay to occupy an important role in mining and geological industries while the high degree of swelling of clays is exploited in construction industries.

iii. clays are widely used as foundry sand-bonds in steel-making industries as well as binding agents in production of iron-ore pellets.
iv. clays take a prominent place in the list of natural sorbents,it is therefore, use to remove heavy metal ions and organic compounds from industrial water.
v. clays are used as adsorbents in food industries
vi. clays are used as binders or fillers in pencil-making (black and colored) industries
vii. they are also used in ceramics industries
viii. they are used as fillers or coatings in rubber and paper industries
ix. clays are used in pharmaceutical, cosmetics, cement, and paint industries etc

For a clay to be suitable in pencil-making, it must have adequate green and dry strength when mixed with graphite and high firing strength. It must be of the type that will not cause splitting during drying and firing and it must be at least semi-refractory. The material must have dimensional stability and yet be sufficiently plastic with graphite to enable extrusion intoproper shape. Further-more the clay most have particle-size distribution compatible with the graphite particles so as to give optimum writability (US patent No. 2986472, 1961). Therefore, the most suitable clay for pencil-making is bentonite.

2.16 Concentration Processes

The physical and chemical characteristics of minerals and rocks are considered in mineral processing to achieve the separation, based on the fact that both the valuable and non-valuable minerals exhibit different behavioural patterns (Fuerstenau and Han, 2003).Some of these properties include: density, electrical conductivity, surface properties, magnetic susceptibility etc. Some of these properties are utilized in the concentration operations of minerals such as:

i. Ore sorting
ii. Magnetic and Electrostatic concentrations
iii. Gravity concentration
iv. Froth flotation

2.16.1 Ore sorting

The beneficiation of an ore by sorting involves inspection and recognition of worth of each particle followed by separation into either a valuable or worthless fraction. Hand sorting is the oldest method of sorting. The success of ore sorting depends on valuable mineral essentially liberated from the gangue at coarse sizes and identifiable by a detector within the residence time. The ore sorters are classified on the basis of the type of detection system used, which include: conductivity, optical and photometric, radiometric and X – ray.

This method of solid – solid separation for minerals utilizes colour differences in some ores detected by naked eye. In some cases, electro – optic detectors collect data on the responses of minerals when exposed to infrared light, visible light, ultraviolet light, laser light and gamma radiation; these can be used in identifying and sorting out minerals. Equipment such as photometric and radiometric sensors can be used in sorting out of minerals (Kawatra*et al*., 2019).

2.16.2 Magnetic and Electrostatic Concentration

(a) Magnetic separation

Magnetic concentration depends on the differences in magnetic susceptibility of minerals utilized in operation. All minerals can be classified into three groups based on their magnetic properties, namely; ferromagnetic, paramagnetic and diamagnetic properties. Paramagnetic minerals exhibit positive magnetism, thereby having a greater magnetic field flux. Diamagnetic minerals exhibit negative magnetism, thereby having a lower magnetic field flux. Ferromagnetic minerals are very strong paramagnetic mineral such as magnetite. The higher the magnetic susceptibility, the higher is the field density in the particle and greater is the attraction up the field gradient towards increasing field strength. Magnetic separation depends on a particle magnetic susceptibility in a magnetic field (Kumar, 2017). The force, F acting on a particle is proportional to the product of the field strength and the field gradient$\left(\boldsymbol{\frac{dH}{dl}}\right)$i.e

$$\boldsymbol{F} \propto \boldsymbol{H}\left(\boldsymbol{\frac{dH}{dl}}\right) \tag{2.1}$$

F is the force on the particle,

H is the field intensity

$\left(\boldsymbol{\frac{dH}{dl}}\right)$ is the field gradient.

Magnetic separators can be broadly classified into the following:

i. low intensity: this is the separator used for ferromagnetic minerals such as magnetite.
ii. high intensity: this is the separator used for paramagnetic minerals.
iii. high gradient separator
iv. superconducting magnetic separator

(b) Electrostatic separation

Some minerals conduct or take an electrical charge on their surface if brought into contact with a source charged to a sufficiently high electrostatic potential. Electrostatic separation applies to only a small number of minerals.

Electrostatic separation depends on differences in the electrical conductivity of minerals and electric field strength required. In Tribo-static separator, the mineral particles are charged by exposing it to high electrostatic potential. Some will take on a positive charge and others a negative charge. These charged particles then pass between charged plates with the positively charged particles attracted toward a negatively charged plate and the negatively charged particles attracted toward the positively charged plate.Tribo-static separation is only effective when the particles are dry and at temperatures greater than 100 – 110^{0}C (Fuerstenau and Han, 2003).

2.16.3 Gravity Concentration

Gravity concentration method uses differences in the density of the minerals to effect separation of one mineral from another. The separation by gravity can be categorized into two methods:

i. Separation in water (gravity concentration)
ii. Separation in a heavy medium (Dense Media Separation)

In jigging during the course of separating a particular mineral via gravity concentration method, there are two actions; one is the effect of hindered settling, meaning that a heavier particle will settle faster than a light particle. The other one is the separation process in an upward flow of water which separates the particles by their density (Moore, 1990; Wills and Napier-Munn, 2006).

2.16.4 Froth Flotation

Froth Flotation is a process for making a solid–solid separation based on differences in the surface properties of minerals (composition and electrical charge). A froth is formed by introducing air into a fine particle slurry (pulp) containing a frothing (foaming) agent and other reagent inside the flotation cell. Particles with air affinity (hydrophobic) are carried by the bubbles to the surface where they are removed by scrapping. These reagents include:

i) Collectors: Reagents used to coat the desired mineral with a hydrophobic coating and allows bubble to attach to the surface of the mineral.

ii) Frothers: Reagents used to create a stable froth, stiff enough to facilitate mineral separation, but not break so as to facilitate subsequent handling.

iii) Modifiers: Reagents used to ensure that the desired mineral float and the undesired mineral sink. These include activator, depressant, pH modifying agents, blocking agents, etc (Moore, 1990; Wills and Napier-Munn, 2006).

2.17 Graphite Beneficiation

Graphite is naturally floatable due to its inherent hydrophobic property. Despite this inherent hydrophobic property of graphite which makes it floatable naturally, the separation of gangue is normally improved by the addition of a small amount of kerosene as a collector and sodium silicate as gangue depressant, and floated with either pine oil or methyl Isobutyl Carbinol(MIBC) as frother. Improving recovery and grade by regrinding middling products usually is ineffective because the graphite will smear over the surface of the gangue on grinding, and make it floatable. Because of this and natural interleaving of mica with flake graphite, it is not possible to produce grades of over 95% by floatation. Super purity graphite is made by chemically leaching out the impurities from the concentrate(Crozier, 1992).

In some graphite concentration processes, its poor flotation selectivity is most probably caused by the cross-pollution effect between fine graphite and gangue minerals. On the other hand, the gangue minerals are quite fine and could be mixed into the flotation concentrate by coating on graphite surfaces, and on the other hand, the graphite itself is greasy and ready to smear on the surface of the gangue minerals. As a result, the cross-pollution effect makes different minerals in the ore possess similar surface properties. Therefore, surface cleaning might be an effective way to improve the floatation selectivity (Aslan, 2007).

2.18Particle Size Analysis

Dynamic Light Scattering (DLS) uses the scattering of Light by particles in motion to measure their particle size and distribution. Generally, when particles are suspended in a liquid, they are not stationary, rather, they are in motion which is called Brownian motion (It is a random motion of the particles dispersed in a liquid in all directions). Brownian motion arises due to collision of particles with the solvent's molecules. Small particles tend to move faster compared with larger ones. The velocity with which the particles move with is called translational diffusion coefficient (D) which is related to the size of particles in Stokes-Einstein equation (Malvern, 2003).

$$d(H) = \frac{kT}{3\pi \eta D} \qquad 2.2$$

d(H) is hydrodynamic diameter which is the particle size

k is Boltzmann constant

η is viscosity of solvent

T is absolute temperature

Hydrodynamic diameter is defined as the diameter of a sphere that has same translational diffusion as coefficient as the particle being analysed.

When the dispersed particles are illuminated with a laser beam, the light beam is scattered by the particles thereby causing the intensity of the scattered beam to fluctuate. This fluctuation is translated over time by a detector, the smaller the particles the higher the frequency of fluctuation and vice versa, as shown in Figure 2.6.

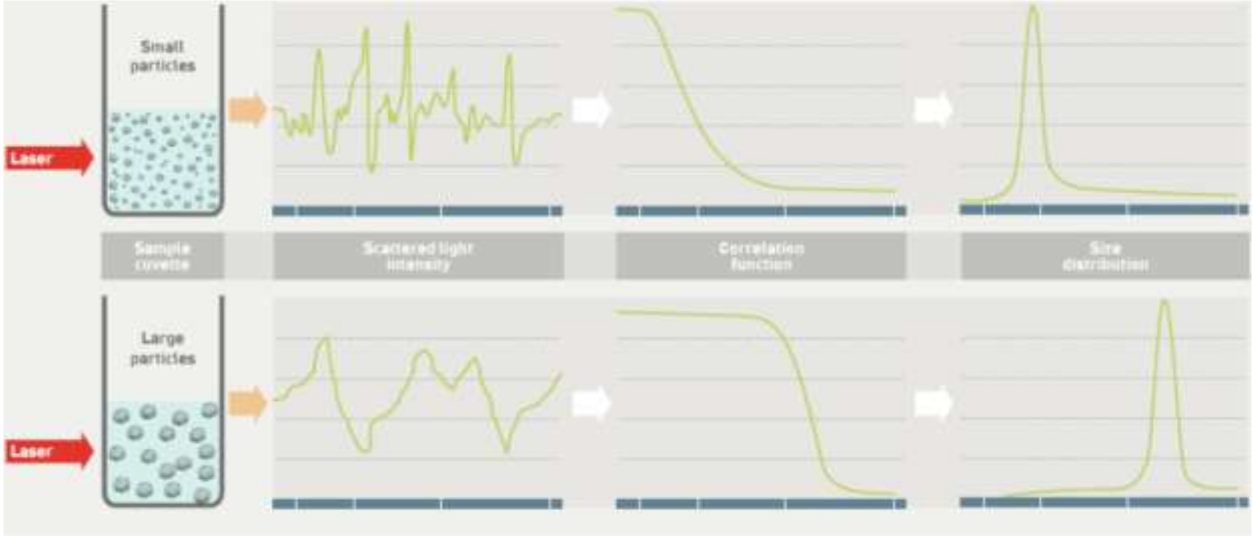


Figure 2.6: Schematic diagram of DLS (*Source*:Malvern.com)

The intensity fluctuation on Figure 2.7 contains the time scale information of particle motion from which translational diffusion coefficient (D) could be derived and used in Stoke-Einstein's equation to derive the particle size (Malvern, 2003).

2.19 Kapok (*Ceiba Pentandra*)

Kapok (*Ceiba pentandra*) is a large deciduous tree, best known for the fibre produced by its fruit. It usually reaches a height of about 30-40 m but some varieties such as *Caribaea*can reach 70 m (Ecocrop, 2011). Kapok has a broad straight trunk and almost horizontally spreading branches. Trunk and branches are supported by prickly buttresses at the base (Orwa *et al*., 2009). Some varieties are covered with rounded spines (Ecocrop, 2011). The leaves are compound (5 to 8 leaflets) (Orwa *et al*., 2009). Kapok produces large quantities of clustered flower, yellowish white to rose, silky and densely hairy on the outer surface. The fruit is a long (10-30 cm) capsule hanging from branches and contains 120-175 rounded dark brown to black seeds embedded in a mass of grey woolly hairs (floss). Kapok is fast growing tree and becomes productive within 4 to 5 years. Yield increase for about 8 years and its economical lifespan is about 60 years. A tree under optimal conditions may yield 330-400 fruits per year, giving 15-18 kg fibre and about 30 kg seeds. A satisfactory fibre yield is about 450 kg/ha and a very good yield is about 700 kg/ha (Louppe *et al.*, 2008).

Kapok fibre is much appreciated for its low density and insulating properties that make it suitable for a large number of commercial applications, including filling for pillows, mattresses and clothes, as well as thermal and acoustic insulation. Kapok wood is a light and resistant timber useful for plywood, packaging, etc. In Java, the tree is grown as a boundary tree and fences along roadsides. In addition to fibre, Kapok seeds contains 20-25% of an oil, very similar to cottonseed oil, that can be used for cooking, to make soap and as lubricant. Kapok flowers are important source of pollen for honey bees (Orwa *et al.,* 2009)

Plate V: Kapok (*Ceiba pentandra*) Tree (*Source*: Orwa et al., 2009)

2.20 History of Writing

With his finger and natural-colored ores, and later on with flint implements, prehistoric man drew pictures of animals on stone and bone. The Chinese used a bamboo pencil, flattened out at one end into a brush-like tip, to write and draw with a colored liquid on bamboo or wooden tablets. Millions of these pen-brushes are still in use. The Egyptians developed a pen-brush of their own, very similar to that of the Chinese, but made of reed and used for writing on papyrus (Enke,1970), as shown in figure 2.9. Papyrus was man-kind's original paper. The Greeks and Romans wrote on wax covered tablets with a metal pointed instrument called a "stylus."

Figure.2.7: Stylus pen (*Source*: Enke,1970)

The quill pen was adopted in the seventh century. It wasmade from hollow wing feathers of birds, and was used for a thousand years by civilized mankind. The Declaration of Independence and some of the greatest masterpieces of literature have been written with quill pens. Graphite, the main ingredient of the modern pencil, was discovered about 1400. At first used without a covering, various devices to hold it were developed by the seventeenth century. Finally, around 1686, a means of putting graphite between strips of wood was discovered and the present-day physical form of the pencil arrived. In 1795, a Frenchman, Jacques Conte, started the modern pencil industry by using clay as the binder to hold the powdered graphite together (Encke,1970).

2.21 Pencil production

Subsequent sub-sections discuss the different aspects involved in Pencil production

2.21.1 Pencil lead production

In pencil lead production, finely ground graphite powder and clay are mixed together with water for about 35minutes mixing cycle taking into consideration; the blending speed, pressure, temperature and moisture level. The mixture is then taken into the hydraulic press to form a cylindrical block which is later wrapped with film to prevent drying out and set aside for a week to cure. Each cured block is charged into a hydraulic press which pushes it into a forming die to produce lead pencils of the required diameter. The lead pencils produced from the forming die are soft and pliable because they contained some certain amount of water and they are therefore, taken into a dryer at 160^oC for 8hours after which they are charge into a kiln at 1000^oC for 10 hours. This helps to transform the clay present in the pencil leads and also strengthen the pencil leads to the final required hardness(Chi,2017).

2.21.2 Pencil casing

Pencil lead casings may either be made from wood, paper, or plastics. In the case of wood, the wood should be soft enough so as to enable continuous sharpening and it should be strong enough to withstand writer’s hand pressure. Normally, cedar as a wood fullfiled such requirement hence it is being used for such application.

2.21.2.1 Pencil casing process

The pencil casing process involves the following steps (Pencils.Com, 2021):

i. The pencil stock(Cedar timber) is cut into pencil blocks which is a bit longer than the normal length of a pencil. The small amount of the extra length is called “trim allowance” (see appendix 3).

ii. The pencil blocks are cut into pencil slats, using specially designed circular saws. These saws are very thin in order to reduce the amount of waste in sawdust. Due to the natural grain and defect characteristics of wood, slats are sorted by width and grade for further processing. Slats without defect are called “full ply”. Some slats are cut to smaller width (called “narrow ply”) or shorter lengths(called “memos”) in other to eliminate the defects and to produce a variety of usable grades and plies of pencil slats (see appendix IV).

iii. The slats produced are then treated with wax and stain to obtain uniform color and improve the machining and sharpening characteristics of the wood for future processing (see appendix IV).

iv. The grooving machine is used to cut grooves into the slats in which the writing core will be placed and glued (see appendix V).

v. A second grooved slat is then glued onto the first making a sandwiches after which the sandwich is clamped and held together tightly while the glue dries (see appendix VI).

vi. Once the glue dries, the sandwiches are then transferred to a shaping machine so as to machine them to pencil shapes which may either be hexagonal or circular (see appendix VII).

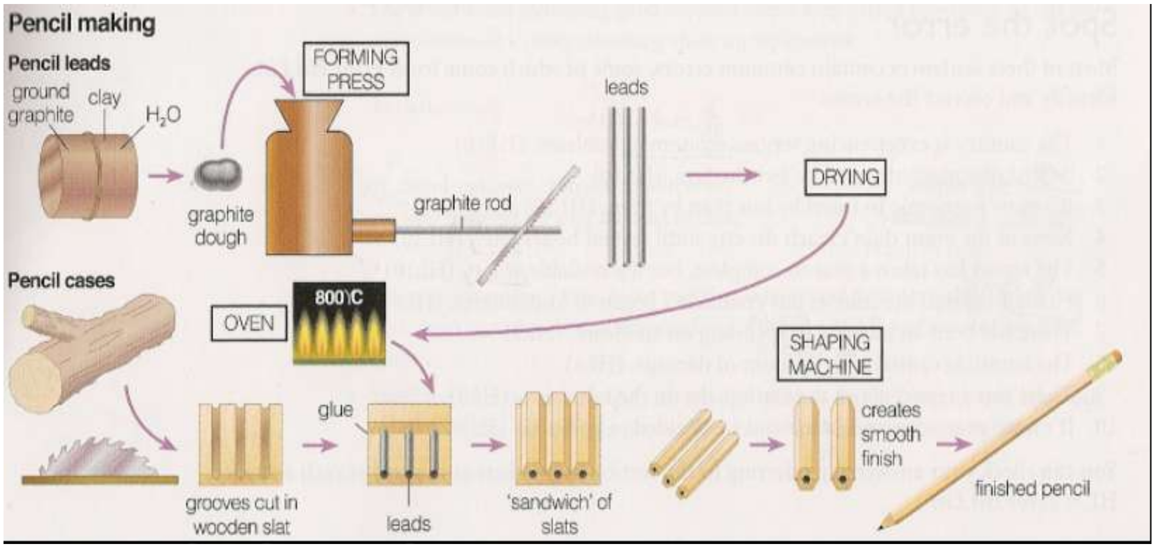


Figure 2.8:Pencil production process(*Source*: Pencil Manufacturing Process-IELTS)

2.21.3 Qualities of a good pencil

A good pencil should have the following properties (Martes, 2020):

i) The pencil leads should be strong enough and should not break while sharpening

ii) The pencil should be light-fast i.e the hue and shade should not fade after a certain period of time and by exposure to sunlight.

iii) The pencil should produce a consistent shade according to its hardness.

iv) The grip should be comfortable enough for longer hours working.

v) Good quality pencil leads do not brake easily and glide smoothly on paper.

vi) The wooden casing should be soft enough so as to ease sharpening and strong enough to prevent bending of the pencil during writing due to the writer's hand pressure.

2.21.4 Factors affecting qualities of a pencil

The quality of a good pencil can be affected by the following (Martes, 2020):

Inhomogeneity in the pencil leads which may affect the hardness and strength of the pencil leads.

i) Uneven/ improper mixing of the mixture of pencil lead constituents (graphite, clay and water) is detrimental to the final properties of the pencil leads as aresultsof inhomogeneity in the pencil leads which is due to the uneven mixing of the mixture.
ii) Moisture level in the pencil leads after firing operation also affects the quality of a pencil
iii) The type of wooden casing
iv) Improper firing of the pencil leads after drying also affects the final hardness of the pencil leads significantly.
v) Clay content in the pencil leads.

2.21.5 Variables in pencil production

The following are the variables considered in pencil production (Martes, 2020):

i) pressure exerted by the hydraulic press
ii) firing and drying temperatures
iii) percentage composition of clay
iv) blending speed, pressure, temperature and moisture level

2.21.6 Extruded pencil casing

Recent pencil production technology has increasingly focused on polymeric materials and how these polymeric materials might be used in pencils. Typically, in a polymeric pencil production process, the pencil casing and its writing material are coextruded. That is to say, the writing material and the pencil casing are extruded from one die which forms both the writing material and its casing. If a sheath is also desired, this may be added as a third element and the extrusion becomes a “triple co-extrusion” or “tri extrusion' process, each component of the pencil being received in the triple co-extrusion die from a different extruder. This polymeric casings can be made to provide the same required properties as that of the wooden casing, such as; good sharpenability, good toughness, good stiffness and also good strength(US patent No. 0022962A1, 2003).

The composition for the extruded Pencil casing include the following:

i. 49.5% Acrynlonitrile butadiene styrene copolymer
ii. 38.5% wood fiber
iii. 5.0%Zinc stearate
iv. 5%Polystyrene maleic anhydride copolymer
v. 2%Polyethylene maleic anhydride copolymer

The polystyrene maleic anhydride copolymer acts as a compatibilizing agent for the polystyrene and the wood fiber to increase the strength of the composite. By compatibilizing, it is meant that the polystyrene maleic anhydride bonds to both the wood fiber and the acrylonitrile butadiene Styrene, thereby acting as a binder within the system. The maleic anhydride constituents along the polystyrene chain bond to the cellulosic fibers of the wood filler which effectively forms a polymeric coating on the wood filler. This polymeric coating on the cellulosic fibers is then available to bond to the acrylonitrile butadiene styrene component of the system thus forming a wood/polymer union. This compatibilizing role of the polystyrene maleic anhydride is thus important in the overall performance of the casing material (US patent No. 0022962A1, 2003)

The sharpneability of pencil casing, be it of wood or polymeri can be determined by some qualitative observations when the sections of the casing are cut and sharpened in a typical sharpener. This is shown in Table 2.2 below.

Table 2.2: Information derivable from a pencil's sharpenability.

Sharpenability	**Observation**
Very poor	Essentially unsharpenable
Poor	Much torque is required, also small fuzzy shavings is observed
Fair	Higher than average torque is required and small fragmented shavings is made
Good	Average torque is required with rolled shavings
Very good	Little torque is required with large continuous shavings

(*Source*: US patent No. 0022962A1, 2003)

2.21.7 Production of pencil leads with uncured Epoxy resin as binder

A pencil lead can be producedwith an uncured epoxy resin as binder instead of clay in the production process, and it is seen that a promising result could be obtained i.e the desirable properties obtained with clay as a binder is also obtained when uncured epoxy resin is used as a binder in the entire process (US patent No. 3834910A1, 1974).

In a preferable embodiment of preparing a graphite lead according to this invention, graphite powder, finely divided powder of the above-mentioned epoxy resin and, if desired, a hardness adjuster are blended by means of a mixer.The resulting powdery mixture is dried at about 80^{o}C and melt-extruded from an extruder in which the maximum cylinder temperature is adjusted within the range of 140 to 180^{o}C.The extruded strands are hot-cut into pellets, and finally the pellets are extrusion molded by means of a lead-forming extruder at the end of which a die having holes of a diameter of 2 mm is mounted, thus, graphite leads are obtained(US patent No. 3834910A1, 1974).

The hardness adjuster may be used in an amount necessary for imparting the desired hardness to the product lead. When the hardness adjuster is not employed, the resulting graphite lead has a hardness of 7H or 8H. Metal soaps are usually employed as such hardness adjuster. Among metal soaps, calcium and aluminum salts of stearic acid and lauric acid are especially useful because they are non-toxic (US patent No. 3834910A1, 1974).

Examples of the mixing ratio of the graphite powder, epoxy resin powder and hardness adjuster are as shown in Table 2.2.

Table 2.3: Mixing ratio of graphite powder, epoxy resin powder and hardness adjuster

Hardness	Graphite(%)	Epoxy resin(%)	HardnessAdjuster(%)
HB	70	12	18
H	70	18	12
4H	70	20.5	9.5
7H	65	35	0

(*Source*: US patent No. 3834910, 1974)

In the case of graphite leads of grade HB or H, it is possible to increase the graphite concentration up to about 75% by weight. However,it is convenient to conduct the melt-kneading of the starting material mixture in an extruder in a manner as described above, but it is also possible to employ a Banbury mixer or roll mill to effect the melt-kneading of the starting material mixture. Furthermore, a part of graphite may be replaced by other black pigment, and various additives customarily used for the production of molded articles of plastics, such as stabilizers and fillers, may be incorporated into the starting material mixture (USpatent No. 3834910A1, 1974).

2.22 Pencil grading

Pencils come in many different varieties. Basic pencils are graded based on the amount of the graphite used in the pencil. The amount of clay mixed with the graphite determines the hardness of a pencil lead as shown in Table 2.4. More graphite means a softer pencil lead;a softer pencil lead leaves a darker mark. The harder the graphite lead, the lighter the mark the pencil makes (Wright, 2018). (See Appendix VIII).

Table 2.4: Graphite, Clay and Water proportions for the entire range of pencil grades

Pencil Lead grade	Graphite (%)	Clay (%)	Water (%)
9H	41	51	5
8H	44	48	5
7H	47	47	5
6H	50	45	5
5H	52	42	5
4H	55	39	5
3H	58	36	5
2H	60	34	5
H	63	31	5
F	66	28	5
HB	68	26	5
B	71	23	5
2B	74	20	5
3B	76	18	5
4B	79	15	5
5B	82	12	5
6B	84	10	5
7B	87	8	5
8B	90	5	5

(*Source:* Sousa and Butchanan, 2000)

2.22.1Soft Pencil Leads

Soft-lead pencils are made with a high graphite-to-clay mixture. Many graphic artist pencils have a thin wax added to the mixture to provide the heavy, soft stroke. If you desire soft, fat stokes, then a soft pencil lead is the choice.

2.22.2 Medium Soft Pencil Leads

Medium soft leads have slightly less clay (24-26%) mixed in with the graphite. The medium-soft pencil lead leaves thinner and lighter stokes. This pencil style is the model parents are asked to buy when selecting school supplies.

2.22.3 Pencil Lead Grades

Pencil leads are graded by the individual manufacturer. There is no industry standard, as each company has its own grading standards. In general, pencils are numbered or graded to inform the buying public of the hardness of the pencil lead. In the United States, most companies use a numbering system of 1 to 4. Pencil leads also have subgrades that are used mainly by graphic artists: 4H, 2H, H, HB, F, B, B2 and the softest being B4 (see appendix 9).

2.22.4 Hardness and Darkness

The higher the number, the harder the lead and the lighter the marking left by the pencil lead. In the United States, the number 4 pencil is the hardest lead grade. Hard pencil leads leave thin stokes and are not recommended for fragile quality paper.

2.23 Previous works done on Graphite and Alawa graphite deposit

RMRDC (2010) reported that the estimated reserve of Alawa Graphite deposit is 1.1-3.3 metric tones. Figure 2.9 shows the Map of Rafi Local Government Area within the context of Niger state where Alawa deposit is Located.

Muhammad *et al.* (2014) characterized Sama-Borkono graphite from Warji Local Government, Bauchi state Nigeria. The graphite was beneficiated using froth floatation method with pine-oil as frother and xanthate as collector, characterised and found to be of high grade and purity. The Carbon content were found to be 46.58 and 95.42wt% before and after beneficiation respectively which is acceptable for pencil production.Itwas also established thatcharacterisation of the beneficiated graphite yielded 95.42% and 91.13% grade for 50µm and 90µm respectively. This suggests that the purity of graphite is dependent on the particle size to some extent; the smaller the sizes the more efficient the beneficiation(floatation). However, a coarse size of 300µm or above and finer size of 5µm or below did not obey this rule.

Keelings (2017)studied properties and uses of south Australian graphite resources. Keelings classified commercial natural sources of graphite into three(3): Flake graphite, Vein or Lump graphite, and Amorphous(microcrystalline) graphite. This classification reflects the geological setting and the condition under which the graphites are formed. Flake graphite(crystalline graphite flakes) has coarse particle size greater than 150µm and fine particle size less than 150µm, Vein or Lump graphite is an interlocking aggregate of coarse graphite crystals typically greater than 4cm, while Amorphous graphite is microcrystalline, soft earthy graphite mostly less than 40µm.

Adeoti *et al*. (2019)determined the work index ofSaman-Borkono graphite using modified Bond's Method. It was established that the work index is 11.047kWh/tonne, considering the economic implication, it shows that, the cost of energy used to comminutte one tonne of the graphite 80% passing 100 microns is N303.79 at a unit cost of N27.5 per energy-being a unit cost of power consumption by industries in Nigeria.

Lee *et al*. (2015)conducted a research on materials and manufacturing process for graphite. He classified graphite into; natural and artificial graphite. the artificial graphite was defined as bulk-graphite, due to its outstanding properties such as; light weight, thermal resistivity, thermal conductivity, electrical conductivity, chemical stability and high-temperature strength. In powdered or bulk form, it has many applications in various industries. Powdered graphite is used in secondry cell anode, while bulk graphite is used in steel-making electrode bars, nuclear reactor moderator, silicon ingot for semi-conductors etc.

Chehreh Chelgani, *et al.* (2016) reviewed graphite beneficiation techniques. It was discovered that a graphite of about 99.99% carbon content can be produced by upgrading the floatation products through chemical (leaching combine with caustic roasting) methods. The caustic roasting (with NaOH) and acid leaching (with HCl/H_2SO_4) producedGraphite of very high purity and also removes impurity even at parts per million (ppm) range. Although this technique allows producing high-grade products, it is costly and generates a large quantity of acid and alkaline waste-water.

Peng *et al*. (2017) studied the possibility of increasing the fine flaky graphite recovery in floatation via a combined multiple treatments technique of middlings. It was established that by adopting a suitable strategy for treatment of the middlings, the graphite recovery increased from 51.81% to 91.14%.

Florena *et al*. (2016) worked on floatability study of graphite ore from southeast Sulawesi (Indonesia). The enrichment ratio of graphite by froth flotation was studied considering the effect of reagents concentrations, rotation speed, and particle size on carbon grade and recovery of the concentrate. It was reported that the optimum conditions for the floatation of the graphite ore is at 1100rpm, -180µm particle size and 9 pH. The carbon grade at this conditions increased from 3% to 60%.

Osasona *et al*. (2019) studied thegrindability of Ningi graphite deposit. It was established that, approximately 39.77kWh/tone of energy is required to reduce one tone of Ningi graphite ore from 80% passing of 415.43µm size to 80% passing of 167.53µm. Therefore, for an efficient and economic comminution design, any piece of mill required to grind Ningi Graphite ore must have a capacity of above 39.77kWh/tone.

Ankit (2018) studied Graphite Flotation and its Kinetics. It was found that, graphite flotation kinetics follows first oder for both MIBC and CRYSTOL frothers. It was also noted that the higher the value of rate constant(k), rate of flotation also become high, therefore, the rate of flotation using MIBC frother is higher than that of CRYSTOL frother.

Nwoke *et al.* (1997) worked on flotation of low-grade Birnin-Gwari and Alawa graphite deposits. Birnin-Gwari and Alawa graphite are amenable to flotation employing Kerosene or combination of Kerosene and Pine oil or refined rubber nut oil as collector while using sodium silicate as depressant and MIBC as frother. High graphite grades and recoveries of >90% and ≥83.9% were achieved using kerosene or combination of kerosene and pine oil. The test with refined rubber nut oil at a 1:1 ratio with kerosene produced a good grade graphite concentrate containing 86.3%C with a recovery of 90.4%C

Akindele *et al.* (2019) optimized concentration parameters for flotation of Alawa Graphite deposit to pencil grade and revealed that the carbon content of the concentrate was 95.4% which is in tandem with the recommended grade of graphite for pencil making. The deposit was found to contain 36.2% of carbon. The optimum processing parameters were found to be; 50µm, 2ml, 2ml, 3ml, 8.5 of particle size, collector, frother, depressant, and pH value respectively. The recovery was also found to be 75.3%.

Based on the literatures reviewed, it can be observed that a lot of works have been done on some Nigerian Graphite in an effort to establish the amenabilityto concentration via froth floatation technique. It is however, clear that the majority of the works focusedon the development of the processing routes and characterization of the Graphite. However, an effort was not made to utilize these deposits in production of some graphitic materials such as Pencils which require less sophisticated technology. It is in this light that this research focused onproduction of pencil leads via the used of designed and developed Pencil extrusion die.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

The materials used in this research include the following; Graphite samples sourced from Alawa, Rafi Local Government, Niger State, Kerosene as a collector, sodium silicate as gangue depressant and Pine oil as a frother, Paraffin Wax, Clay- samples, Lime, Granite and mild-steel.

3.2 Equipment

The equipment/tools/apparatus used in the course of this research include the following;

i. Laboratory jaw crusher(415v,50Hz,4000w & 8.1A)
ii. Pulverizer(220-240V, 50Hz, 370w & 2x3.8A)
iii. Set of sieves(British Standard Test Sieve)
iv. Laboratory sieve shaking machine(220-240V, 50Hz, 80w & 2.3A)
v. Weighing balance
vi. Denver froth flotation machine (Denver D12, 0.18kw 50Hz)
vii. Ball-mill
viii. Furnace
ix. Mixing machine
x. Hydraulic press
xi. Lathe machine
xii. Extrusion die
xiii. Vickers Micro Hardness Testing Machine (MV1-PC)

3.3 Methods

3.3.1 Sample collection

100Kg of Alawa graphite was obtained by sampling from three different points around the study area; Alawa, Rafi local government area of Niger State. The sampling methodadopted was “Grab sampling” which involves taking portions of ore at random from muck piles, chutes or the top of cars of ores. Figure 3.1: is the map of Alawa, within the context of Niger state of Nigeria, showing the sampling points as obtained with the help of Global Positioning System (GPS).

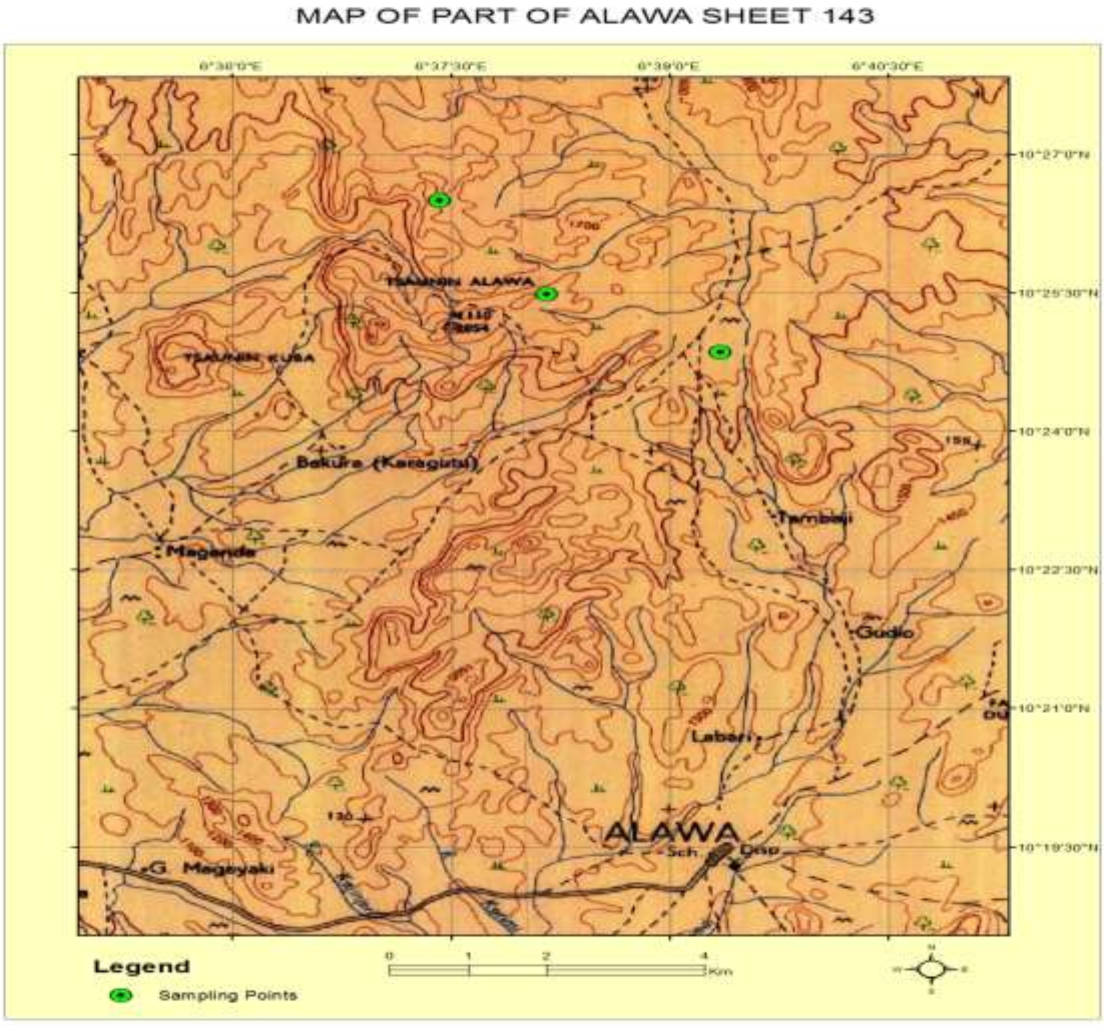


Figure 3.1: Topographical Map of Alawa showing the sampling points

3.3.2 Sample Preparations (crushing and grinding)

The collected samples were mixed, crushed manually with a sledge hammer to attainthe required standard feed size (60mm) acceptable by the laboratory jaw crusher. The samples were crushed and ball-milled, then coned and quartered to obtained a representative sample.

3.3.3 Concentration process

The concentration processadopted wasFroth Flotationona 12D Denver laboratoryFlotation machine to effectively produce the mineral concentrate. The Impeller speed of the machine was kept constant at 1500 rpm for both conditioning and flotation. The pulp was mixed for three minutes prior to addition of collector (Kerosene) and after an additional mixing of three minutes, the frother (Pine Oil) was added. After three-minute mixing period, air was introduced into the cell and the froth products were collected for five minutes.The optimum amount ofcollector,depressant and frother used were; 2ml, 3ml and 2ml respectively at a pH 8.5,as established byAkindele *et al*.(2019).

3.4 Characterization of the concentrate

The produced concentrate was characterized by proximate analysis to confirm the percentage of fixed carbon, moisture content, ash content and volatile matters.

3.4.1 Proximate Analysis

Proximate analysis was carried out to reveal the percentage of fixed carbon by determining the percentage of moisture, volatile matter and ash content of the sample as follows:

i. Moisture content analysis

   The moisture content was determined using the standard procedure of ASTM C56. A known weight of graphite concentrate samplewas placed in a silica crucible and heated in electrical oven for 30 minutes at 110^{o}C after which was removed, cooled and weighed. The moisture content is calculated thus;

$$\text{Moisture \%} = \frac{weig\,ht\ of\ grap\,hite\ sample\ \ before\ \ heating - \text{weight of heated sample}}{weig\,htofgra\,phitesampletaken}\, x100 \qquad (3.1)$$

ii. Volatile matter

The volatile matter was determined using the standard procedure of ASTM 3175. A known weight of moisture free graphite samplewas placed in a silica crucible, heated in Muffle furnace for 9 minutes at 900^{o}C, cooled and weighed. The volatile matter is calculated thus;

$$\text{VM (\%)}=\frac{weig\,ht\ of\ moisture\ \ free\ \ sample\ -weig\,ht\ of\ \ sample\ \ heated\ \ at\ 900\ oC}{weig\,htofgrap\ \ hitesampleused}\text{x100} \quad (3.2)$$

iii. Ash content

The ash content was determined using the standard procedure of ASTM C561. A known weight of graphite sample was placed in asilica crucible, heated in Muffle furnace for 30 minutes at 700^{o}C, cooled and weighed. The Ash content is calculated thus;

$$\text{Ash content \%} = \frac{weig\,htofsample\ \ taken\ -weig\,ht\ of\ \ sample\ \ heated\ \ at\ 700\ oC}{weig\,htofdrygrap\ \ hitetaken}\ \text{x 100} \quad (3.3)$$

iv. Fixed Carbon (FC)

Determination of fixed carbon was done by deducting the sum total of moisture, volatile matter and ash percentage from 100. The fixed carbon is calculated thus;

$$\%\,fixedcarbon = 100 - \ (\%\,moisture + \%\,volatilematter + \%\,ash) \quad (3.4)$$

3.5 Determination of some physical properties of the concentrate

Some physical properties of Alawa graphite concentrate were determined via the following method.

3.5.1 Color and Luster

The colour of the mineral was easily seen without the aid of any optical instrument. Also, the lustre nature of the mineral was determined by physical observation.

3.6 Particle size analysis and Ball-milling

Dynamic Light Scattering (DLS) was used to determine the particle sizes ofAlawa graphite concentrate, Bentonite clayand ball-milled Alawa graphite. 0.05mg of each sample that wasanalyzed was dispersed in distilled water and filtered. The filtrate was placed in Zeta-potential plastic cuvette. Air bubbles inside the cuvette were removed and the cuvette was placed into the analysis chamber for the analysis.The test was run three times and the average was takenas representative particle size.

3.6.1 Ball-milling of Alawa graphite

After analysing the particles size of Alawa graphite concentrate, it was discovered that the particles sizewaslarger compared with thatof the clay that was used. Therefore, for proper writability of the final product, there should be conformity between the particles size of Alawa Graphite and Bentonite Clay.To achieve this, Alawa Graphite was ball-milled for 12 hours using three Ceramic balls of 39.54mm, 29.91mm and 22.48mm respectively at a speed of 100rpm.

3.7 Design and Development of Pencil Leads Extrusion Die

The extrusion die shown inFigure 3.3 was used in this research; itwas designed using Solid-works, e-Drawing 2013 version.Mild-steel was used to develop the Die considering it machinability and yield strength. It was designwith four (4) different components that can easily be assembled together,the components are shown inFigures 3.3-3.7. Two different nozzles with 3and 5mm diameters were designed so as to enable production of Pencil Leads with two different diameters. However, the extrusion die was designed in a manner in which the nozzle could be easily replaced with another of different size, when an extrudate of different diameter is needed. Theassembled components are held firmly by a screw on one side of the jig while the rammer was designed with a small allowance (about 0.15mm) so as to prevent the flowing up of fed materials out of the die.

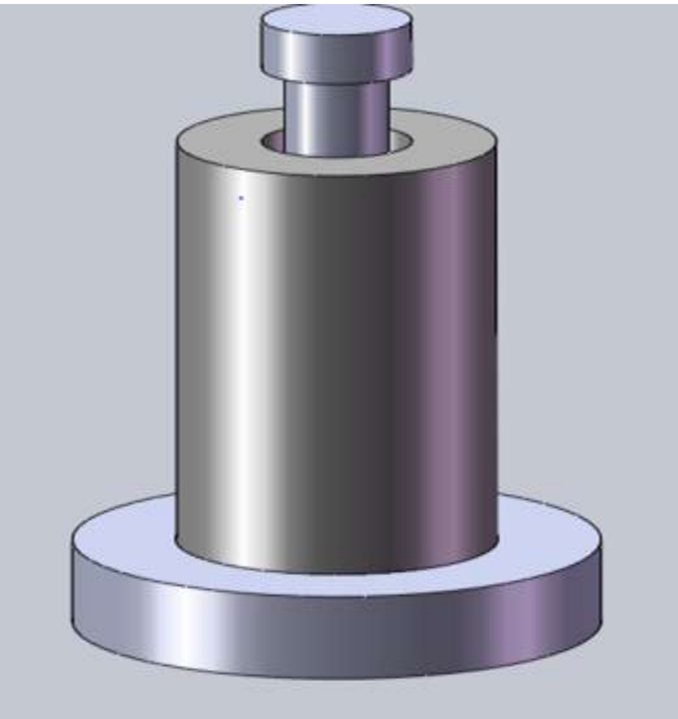


Figure 3.2a: Pencil Leads Extrusion Die

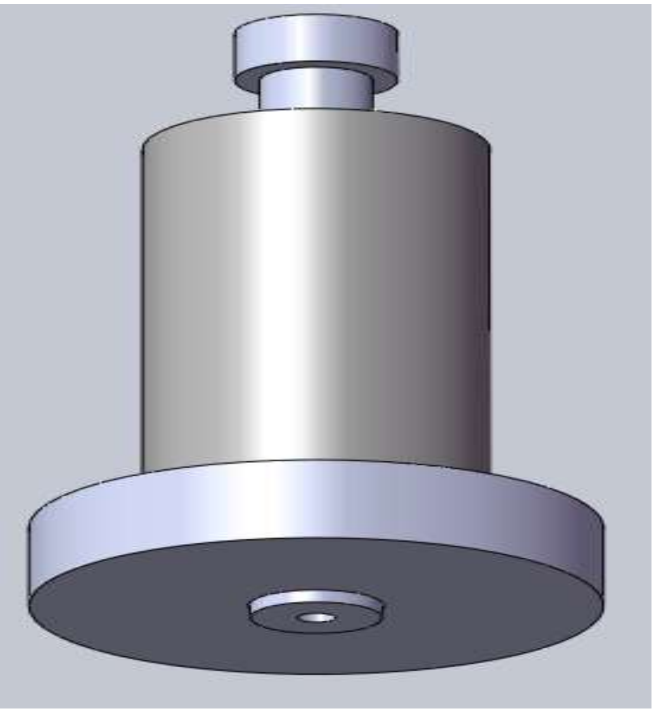
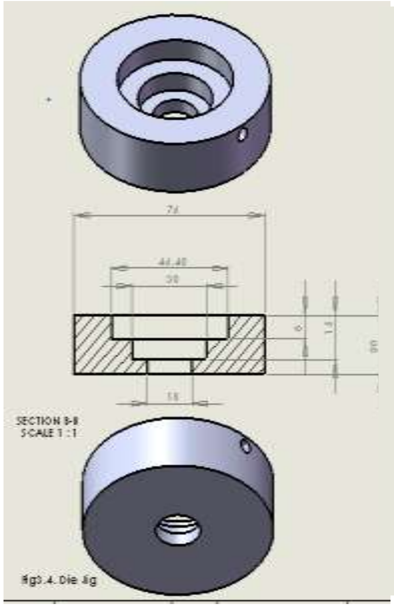
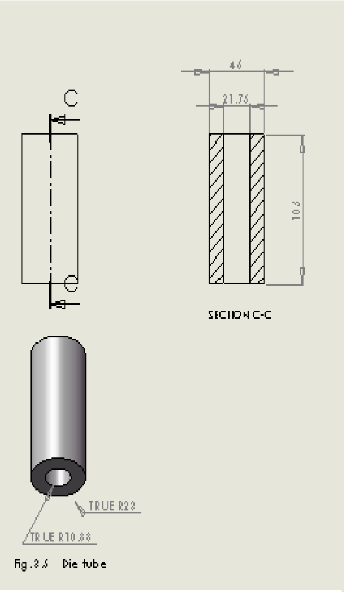


Figure 3.2b: Pencil Leads Extrusion Die





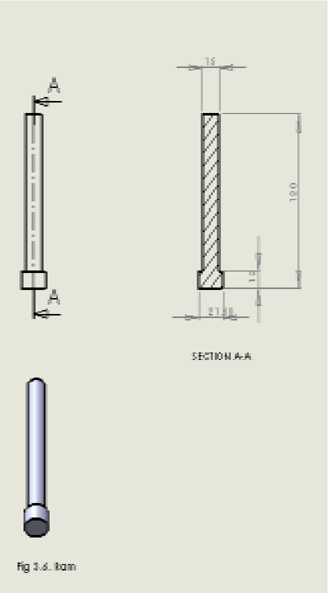
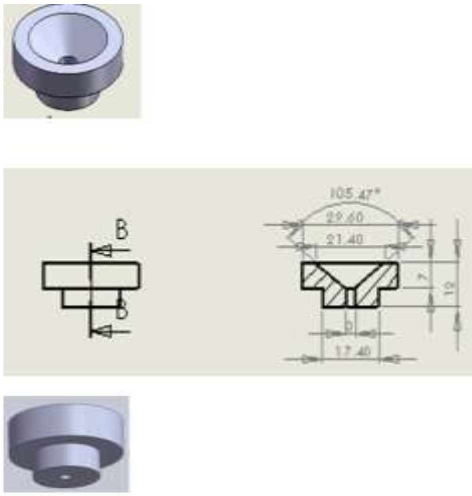


Figure 3.3: Die-jig

Figure 3.4 Die-tube

Figure 3.5: Rammer



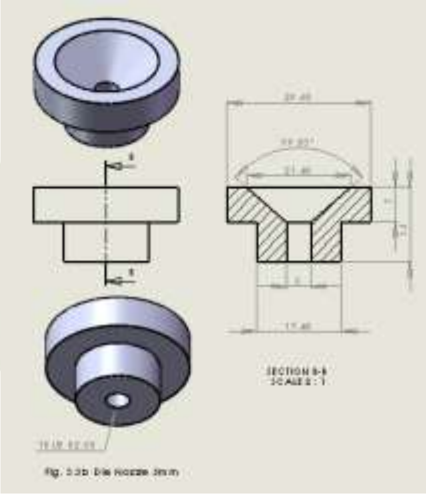


Figure 3.6a Die-nozzle 3mm

Figure 3.6b Die-nozzle 5mm

Figure 3.8 below is an exploded view of the developed Pencil Leads extrusion die illustrating the way in which nozzle could be placed and a screw hole on one side.

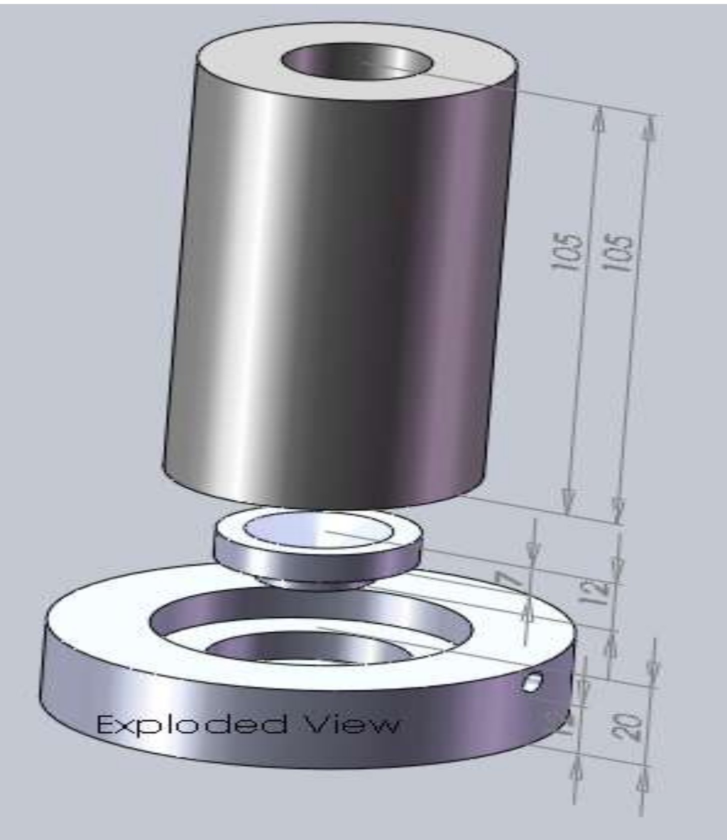


Figure 3.7: Exploded view of Pencil Leads Extrusion Die

3.8 Pencil Leads Production

Pencil leads of HB grade were produced by mixing 67g, 28g and 12.5g of graphite, clay and water respectively. While 6H grades were produced by mixing 50g of graphite,50g of clay and 12.5g of water for about 35minutes mixing cycle until homogeneous granules as shown inFigure 3.9. The resulting mixtures were pressed by Hydraulic press, through the application of 21 kN & 12.4 kN to obtain cylindrical blocks. The blocks were wrapped properly with film and cured for a week. The cured blocks were loaded into anextrusion-die and Pencil Leads of 3 mm diameterwere produced as shown in Figure 3.11. Pencil Leads produced from the forming die were soft and pliable because they contained some certain amount of moisture.

Figure 3.8: Mixture of Alawa Graphite & Clay for HB Pencil grade.

Figure 3.9: Cylindrical blocks produced from Alawa Graphite & Clay mixture for HB pencil grade

Figure 3.11: HB grade Pencil Leads made from Alawa graphite

3.9 Heat Treatment (Drying)

In order to dry the Pencil Leads, the extrudates wereOven-heated at160 ^{o}C for 10 hours, followed by heating in a furnace at a temperature of 600 ^{o}C for 8 hours;this helped to strengthen the Pencil Leads.

3.10 Vickers Micro-Hardness Test

Vickers Micro Hardness tests for the standard Pencil stock and Leads were conducted. Similarly, Micro Hardness tests for the produced Pencil Leads and wood (Pencil Stock) intended for Pencil case were conducted. 20mm×10mm×10mm samples of Kapok and Cedar woodswere obtained using a Tri-square and Hacksaw. Each sample was ground using a grit paper (P600), while a standard HB Pencil Lead of 3mm diameter and a produced Pencil Lead of 5mm diameter were used for the Micro Hardness test. A diamond (Pyramidal) indenter was used with a load of 0.3kgf and maximum and minimum limits of 100HV and 010HV respectively.

3.11 Pencil Casing Production

A soft wood (pencil stock) from Kapok (*Ceiba pentandra*) timber was cut into Pencil blocks. They were then treated with waxto improve the machining and sharpening characteristics of the wood and later cut into slats, onto which groves wereformed. Writing core (Pencil Lead) was placed and glued together.The Second grooved slat was placed on top of the slat glued with writing core and fastened together to make a sandwich, clamped and held together tightly until the glue dried. After the glue dried-up, the sandwich was taken to a Shaperto machine it into pencil shapes.

3.12 Pencil Integrity Assessment

In order to examine the gliding nature and writability of the Alawa Graphite Pencil, it was used to write a short note on a piece of paper and compared with a written short note made with a standard HB Pencil.

CHAPTER FOUR 4.0 RESULTS AND DISCUSSION

4.1 Physical Examination

The visual examination of the Alawa graphite was carried out to identify some of its physical properties. The results of the investigation of some physical properties of the graphite are contained in Table 4.1.

Table 4.1: Some Physical Properties of Alawa Graphite

Property	**Feature**
Colour	Grey black
Streak	Black
Lusture	Shiny
Specific gravity	2.19

4.2 Proximate analysis of the concentrate

The Alawa Graphite concentrate was analyzedvia proximate analysis in order to determine the percentage of fixed Carbon, Moisture content, Volatile matter and Ash content. The result is contained in Table 4.2

Table 4.2: Result of Proximate Analysis

	Moisture content(%)	**Volatile matter (%)**	**Ash content (%)**	**Fixed carbon (%)**
Alawa concentrate	0.43	0.62	3.22	95.73

The percentage of fixed Carbon (FC) was found to be 95.73% which is a suitable Graphite grade for pencil production as reported by Indian Mineral Review (2015).

4.3 Particle size analysis using Zeta-sizer Nano.

The results of the particle size analysis conducted with Zeta-sizer Nano, based on the principle of Dynamic Light Scattering (DLS) is shown in Figure 4.1. The average particle size of 74.7% of the Bentonite Clay sample is 0.15µm(Peak2) while that of 21.6% and 3.7% of the sample is 0.055µm (Peak1) and 0.42µm (Peak3) respectively. Particle size analysis of Alawa Graphite concentrate conducted under the same condition shows that the average particle size of 55.5% of the sample is 1.01µm(Peak2) while that of 44.5% of the material is 0.15µm (Peak1) as shown inFigure 4.2.

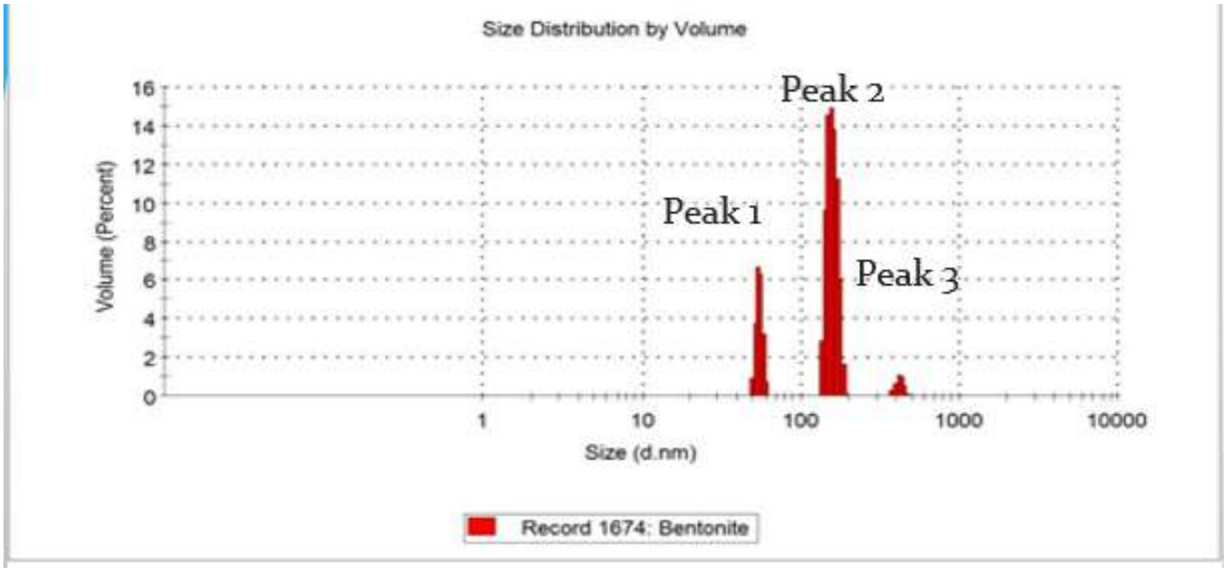


Figure 4.1:Size distribution by volume of a Bentonite Clay sample obtained via Dynamic Light Scattering using water as a dispersant.

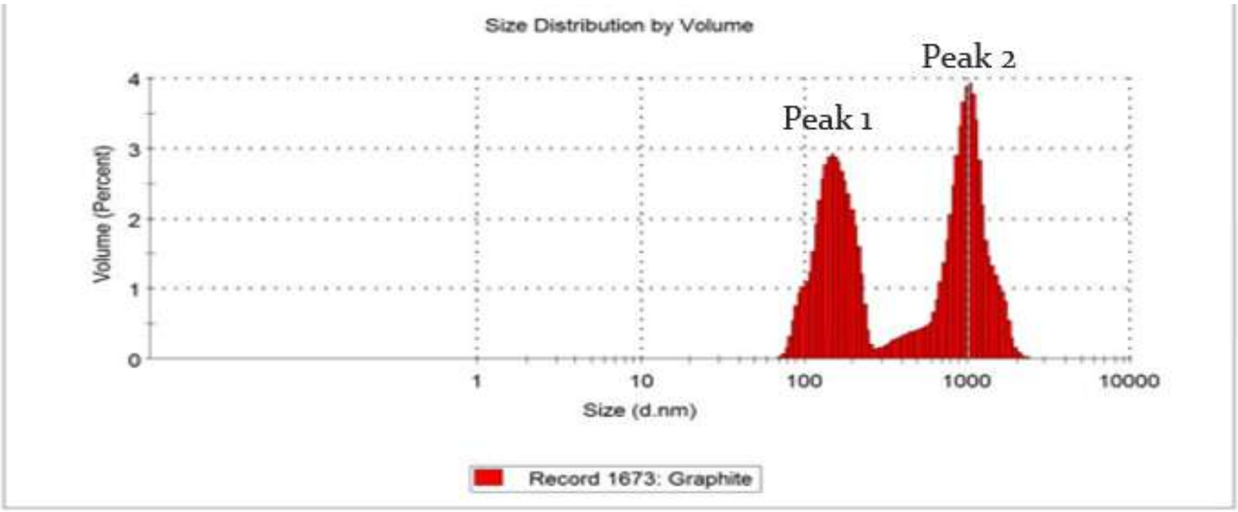


Figure 4.2: Size distribution by volume of as-concentrated Alawa Graphite concentrate obtained via Dynamic Light Scattering using water as dispersant.

From the results of particle size analysis obtained it can be clearly seen that the average particle sizeof 55.5% of Alawa Graphite is 1.01µmwhich is much larger than 0.15µm average particles size of the Bentonite clay sample. However, for optimum writability of Graphite Pencil Leads, there should be conformity between the particles size of the Graphite and Clay(US patent No. 0022962Al, 2003). In order to ensure the conformity between the particles size of Alawa Graphite and Bentonite clay, Alawa graphite concentrate is ball-milled for 12 hours so as to reduce the particles size to very close or equal to that of Bentonite clay. The result of particle size analysis conducted on the ball-milled Alawa Graphite, Figure 4.3 shows that the average particles size of 87.2% of the ball-milled Alawa graphite is 0.23µm (Peak1), which shows that 87.2% particles size reduction was achieved hence the graphite was more suitable for Pencil Leads production with regards to particles size conformity. The import of conformity/compatibility between Graphite& Clay particleswas established by (US patent No. 0022962A1, 2003).

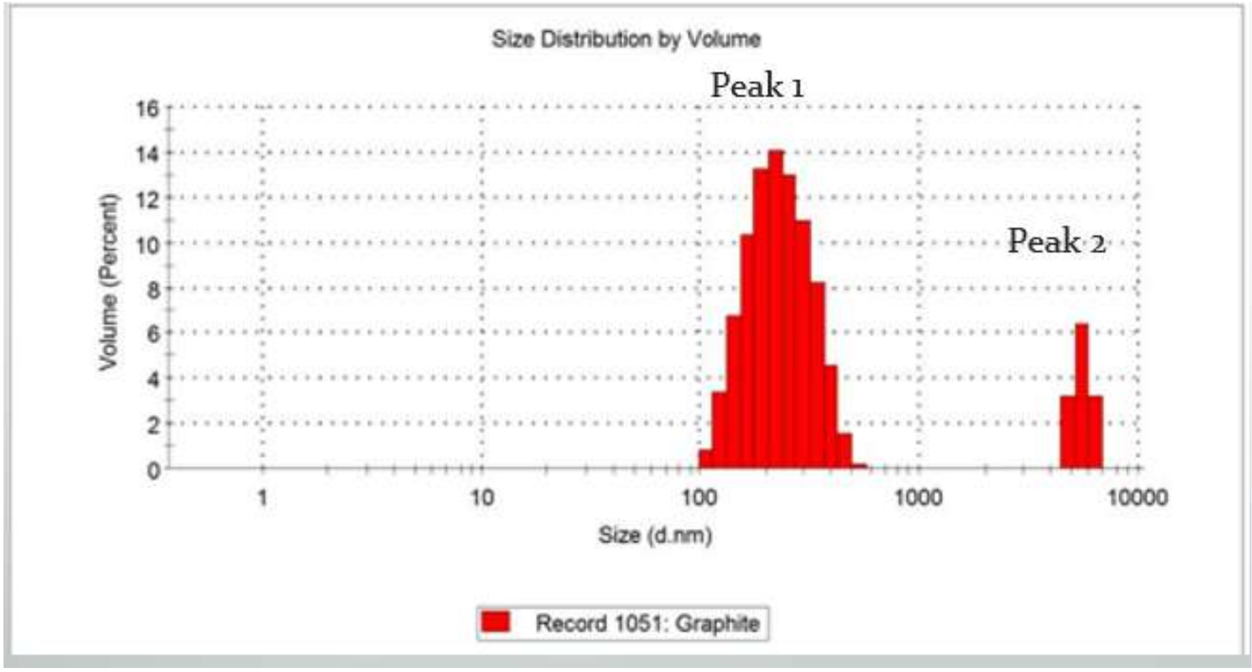


Figure 4.3: Size distribution by volume of ball-milled Alawa graphite concentrate.

4.4 Vicker's Micro-Hardness Tests

Table 4.4 shows the results of the Vickers Micro-Hardness Test obtained for the standard Pencil Leads, stocks and Alawa & Kapok stock.

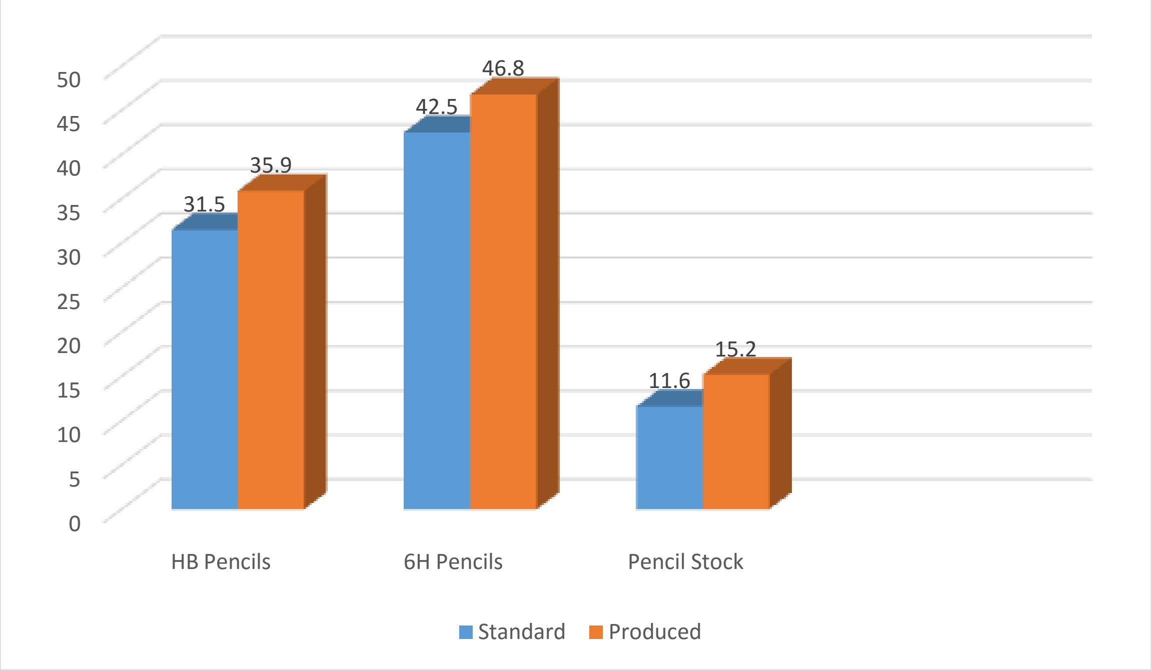


Figure 4.4: comparism ofthe Hardness values of somestandard Pencils Leads, standard Pencil Stock and Alawa Graphite Pencil Leads and Kapok Pencil Stock respectively.

From Figure 4.4, it was observed that the hardness values of HB and 6H Pencil grades produced from Alawa graphite are slightly greater than the hardness values of standard HB and 6H grades Pencil. However, a HB or any other Pencil grade produced from a particular graphite source may not necessarily be the same as the one produced from a different graphite source as this may be as a result of difference in the geomorphology of the individual graphite deposits. Therefore, a HB Pencil produced from a China graphite source may be lighter or darker from HB Pencil produced from England graphite source as reported by Pencil.com (2021).

Kapok timber (*Ceiba pentandra*) with Hardness value of 15.2 HV was satisfactorily used as Pencil stock, though its hardness value is greater than that of standard Pencil stock (11.6HV).

Kapok was found to have good machining & sharpening characteristics which is an important requirement for a candidate Pencil stock as established by Kaygin *et al*. (2015).

4.5 Pencil case

The groove made on the Pencil Slat produced from Kapok (*Ceiba Pentandra*) local Pencil stock is shown on Figure 4.5, while Figure 4.6 shows a Slat glued with Alawa graphite Pencil Lead. Figure 4.7 shows the Pencils produced from Alawa graphite and Kapok timber.

Figure 4.5: Grooved Slat

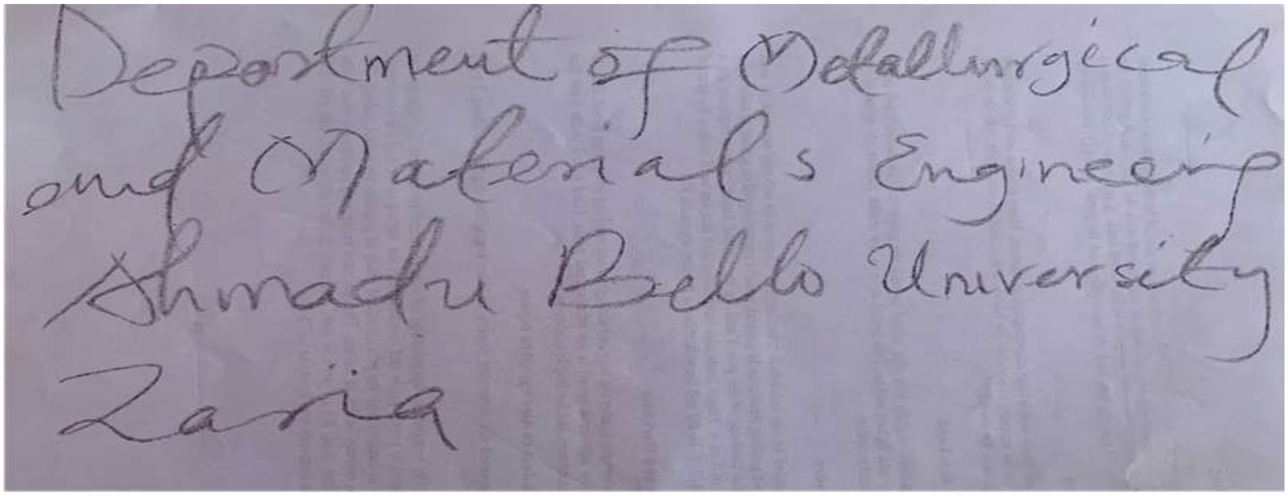
Figure 4.6: Pencil Lead glued together

.

Figure 4.7: Pencils Produced from Alawa graphite and Kapok local pencil stock

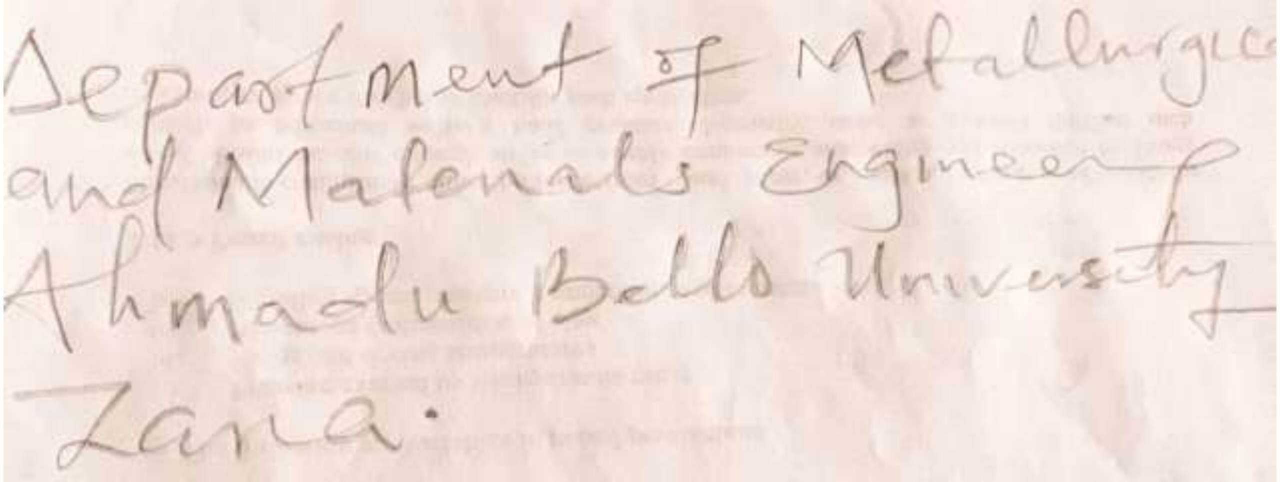
4.6 Writability and Glide Test

It was observed that the Alawa graphite Pencil glides smoothly and also the writability is good compared with the standard HB grade Pencil.



Department of Metallurgical
and Materials Engineering
Ahmadu Bello University
Zaria

Figure 4.8: Ashort notewritten with Alawa Graphite Pencil



Department of Metallurgic
and Materials Engineering
Ahmadu Bello University
Zaria.

Figure 4.9: A short note written with standard HB Pencil

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The study examines the amenability of Alawa graphite to Pencil-making and also the suitability of a Nigerian wood Kapok timber (*Ceiba pentandra*) to Pencil case production.

Based on the results obtained, the following conclusion were made;

i. It was revealed that about 55.5% of Alawa Graphite is of 1.010µm while 44.5% of the graphite is of 0.154µm. The concentrate grade is in alignment with the recommended grade for Pencil making as established by Indian Mineral Review, 2015.

ii. Pencil Leads extrusion die was designed using Solid-works e-Drawing version 2013 and developed. The extrusion die was used to produced Pencil Leads successfully.

iii. Pencil Leads and case were produced using conventional press and dry method.. The Hardness values of the HB & 6H Pencil Leads and Pencil Stock were tested using Vickers Micro-Hardness Tester, and were found to be 35.9HV, 46.8HV and 15.6HV respectively.

iv. The integrity of the Alawa graphite Pencil was assessed by comparison with standard HB Pencil. It was also used to write a short note on a paper so as to assess its writability and gliding nature.Eventually, it was observed that the Pencil glides smoothly and also the writability was good.

5.2 Recommendations

Based on the work carried out, the following recommendations are made:

i. Alawa graphite is suitable and could be utilized for commercial pencil making; hence it is recommended for use as raw material for Pencil production;

ii. Favorable policy and investment opportunity should be put in place by the government for Pencil production;

iii. Kapok timber (*Ceiba pentandra*) could be utilized as a raw material for Pencil making;

iv. The potentials of other Graphite deposits should be evaluated with a view to utilizing them in Pencil production and other uses.

5.3 Contribution to Knowledge

i. It was discovered that the size distribution of the Alawa graphite concentrate ranges from 0.154μm to 1.01μm.

ii. It was also discovered that for Alawa graphite concentrate to be use in Pencil making, it needs to be ball-milled for 12 hrs using three balls of 22, 30 and 40mm diameters respectively.

iii. The extrusion force/pressure with which the HB and 6H Pencil grades were extruded were found to be 21kN and 12.4kN respectively.

iv. The hardness values of Alawa graphite HB and 6H Pencil Leads were found to be 35.9HV and 46.8HV while that of Kapok local Pencil stock was found to be 15.6HV

REFERENCES

Abdou, M.I. & Ahmed, H.E. (2011). The compatibility of egyptian bentonite during drilling shale formations.*Petrol. Sci. Technol*., 29(1), 59-68

Adeoti, M.O., Dahunsi, O.A., Awopetu, O.O., Aramide, F.O., Alabi, O.O., Johnson, O.T, and Abdulkareem, A.S., (2019), " Determination of Work Index of Graphite From Saman_Borkono (Bauchi) Using Modified Bond's Method. *Nigerian Journal of Technology*, Vol. 38, No. 3, July 2019, pp. 609-613

Akindele, U.M., Yaro, S.A., Kasim, A., Asuke, F., and Umar, A.H. (2019). Optimization of concentration parameters for flotation of Alawa Graphite to pencil grade. *Nigerian Research Journal of Engineering and Environmental Sciences*, 4(1), 302-308.

AMG Graphite 2015. Investor Day-AMG graphite presentation- June 2015 AMG, United States, viewed July 2017, <https//amg-nv.com/investors/presentations/>.

Aslan, N., Cifci, F., and Yan, D. (2007). Optimisation of process parameters for producing Graphite concentrate using RSM. *Elsevier B.V.* doi:10.1016/j.seppur.2007.05.022

Atsuhiko, M., and Yoshio, M. (1974). Pencil Lead. Office, US Patent No. 3834910, issued Sept. 10, 1974.

Bergaya, F. &Lagaly, G. (2000). General introduction: clays, clay minerals and clay science. Bergaya, F., Theng, B. K. G. & Lagaly, G. (Eds.), Handbook of Clay Science. Elsevier, Amsterdam, pp. 1–18.

Beaufort, D., Cassagnabere, A., Petit, S., Lanson, B., Berger, G., Lacharpagne, J.C. & Johansen, H. (1998) Kaolinite-to-dickite reaction in sandstone reservoirs. *Clay Minerals*, 33, 297 – 316

Beyssac, O., Rouzaud, J.N., Goffe, B., Brunet, F. and Ghopin, C. (2002). Graphitization in a high-pressure, low-temperature metamorphic gradient: a Raman microspectroscopy and HRTEM study. *Contributions to Mineralogy and Petrology* 143:19–31.

Billmeier, F.W. & Saltzman, M. (1981) Principles of Color Technology, 2nd edition. Wiley Interscience, New York, pp. 1– 23.

Chehreh-Chelgani, S., Rudolph, M., Kratzsch, R., Sandmann, D., & Gutzmer, J. (2016). A Review of Graphite Beneficiation Techniques. *Mineral Processing and Extractive Metallurgy Review*, 37:1, 58-68. doi: 10.1080/08827508.2015.1115992.

Christidis, G.E., Makri, P. & Perdikatsis V. (2004) Influence of grinding on the structure and colour properties of talc, bentonite and calcite white fillers. *Clay Minerals*, 39, 163– 175.

Christidis, G. & Scott, P.W. (1997) Origin and colour properties of white bentonites: A case study from the Aegean Islands of Milos and Kimolos, Greece. *Mineralium Deposita*, 32, 271– 279.

Christidis, G.E. (1995) Mechanism of illitization of bentonites in the geothermal field of Milos Island, Greece. Evidence based on mineralogy, chemistry, particle thickness and morphology. *Clays and Clay Minerals*, 43, 567–594

Christidis, G.E. (2001) Formation and growth of smectites in benotnites: a case study from Kimolos Island, Aegean, Greece. *Clays and Clay Minerals*, 49, 204– 215.

Chung, D.L. (1987). Exfoliation of graphite. *Journal of Materials Science*, 22:4,190–4,198

David, G. C., and Jacob, L. (2003), "Composition for Extruded Pencil Casings and Pencil made Therefrom." Office, US Patent No. 0022962A1, issued January 30, 2003

Dayi, A.M., El-Nafaty, U.A., Bugaje, I.M. (2017) Characterization of Graphite from Sama-Borkono, Bauchi State. *International Journal of Recent Development in Engineering and technology*.

Delhaes, P. (2001).*Graphite and Precursors*. CRC Press. *ISBN* *90-5699-228-7*

de Paiva, L.B., Morales, A.R. & Valenzuela Diaz, F.R. (2008) Organoclays: properties, preparation and applications. *Applied Clay Science*, 42, 8–24

Dobb, M.G, Guo, H., Johnson, D.J., and Par, C.R. (1995). Structure-compressional property relations in carbon fibres. Carbon, 33, 1553. http:// dx.doi.org/10.1016/0008-6223(95)00114-S

Ecocrop, (2011), Ecocrop Database. FAO. http://ecocrop.fao.org/ecocrop/srv/en/home

Ecoport ,(2011). Ecoport database. Ecoport, http//www.ecoport.org

Erich, S. (1935). Process of making writing pencil lead. Office, US Patent No. 2013584, issued Sept. 3, 1935.

Ewais EMM 2004. Carbon based refractories. *Journal of the Ceramic Society of Japan* 112:517–532

Falconer, J.D. and Raeburn, C. (1923). The Northern Tin Fields of Bauchi Province. Geological Survey of Nigeria, Bulletin No. 4.

Florena, F.F., Syarifuddin, F., Hanam, E.S., Trisko, N., Kustiyanto, E., Enilisiana, Rianto, A., Arinton, G. (2016), Floatability Study of Graphite Ore from Southeast Sulawesi (Indonesia). AIP Conference Proceedings, Vol. 1712, issue 1

Frederick, L.E. (1970). The chemistry and manufacturing of the lead pencil, *Journal of chemical education.* Vol. 47, No. 8.

Fuerstenau C. M. and Han N. K. (2003): Principles of Mineral Processing, *Society for Mining, Metallurgy, and Exploration*, U. S. A

Gates, W. P., Anderson, J. S., Raven, M. D. & Churchman, G. J. (2002). Mineralogy of a bentonite from Miles, Queensland, Australia and characterisation of its acid activation products. App. *Clay Sci*., 20(4–5), 189–197

Geological Survey of Nigeria, (1974). Geological Map of Nigeria. 1:2,000,000 Geological Survey Department, Nigeria.

Ghilotti D 2016. Graphite – the only way is up. Industrial Minerals, December 2016 – January 2017, pp. 26–31.

Gleason, M. H., Daniel, D. E. & Eykholt, G. R. (1997). Calcium and sodium bentonite for hydraulic containment applications. J. Geotech. Geoenviron. 123, 438-445.

Grim, R. & Guven, N. (1978). Bentonite: Geology, Mineralogy, Properties and Uses. *Elsevier Science Publishing Co., Inc.*

Grimshaw, R.W. (1971) The Chemistry and Physics of Clays. Wiley-Interscience, New York.

Gu¨ven, N. (1992a) Molecular aspects of clay-water interactions. In: Clay-Water Interface and its Rheological Implications (N. Gu¨ven, R.M. Pollastro, editors). CMS Workshop Lectures, vol. 6. The Clay Minerals Society, Boulder, Colorado, USA, pp. 2 –79.

Himenez, P.C. & Rajagopalan, R. (1997) Principles of Colloid and Surface Chemistry, 3rd edition. Taylor and Francis, New York, pp. 145– 192.

Idongesit, A. (2017). Nigeria spends N750b yearly on pencil importation.Retrieved from https:// www.independent.ng.

Inagaki, M. (2001). Applications of polycrystalline graphite. In Delhaes P, ed. Graphite and Precursors, Gordon & Breach, Amsterdam, 179

Indian Mineral Review (2015). Graphite, Government of India. Ministry of Mines. 53rd Edition

Jacques, B., Philippe, C., Guy, C., Jose, D., Claude, F., Didier, L. (1993). Process for manufacturing pencil by tri-extrusion and the produced pencil having an intermediate protective casings. US patent No. 5244297, issued Sept. 14, 1993.

Jacques, E.A., (1943), Duchin Hai Graphite Schist, GSN Report 783 (unpublished), Geological Survey of Nigeria, Kaduna. pp 2.

Jean, E.D.E. (1927). Process for Purifying, Enriching, or Refining Crude Graphite. Office,US Patent (Ed.). U.S. Patent No. 1614352, issued January 11, 1927.

Jepson, W.B. (1984) Kaolins: their properties and uses. *Philosophical Transactions of the Royal Society, London,* A311, 411– 432.

Jones, B.F. & Gala´n, E. (1988) Sepiolite and palygorskite. In: Hydrous Phyllosilicates (Exclusive of Micas) (S.W. Bailey, editor). Reviews in Mineralogy, 19. *Mineralogical Society of America, Washington D.C.*, pp. 631 –674.

John, K. (2017). Graphite properties, uses, and south Australian resources. *MESA journal*, 84-issue 3

Kawatra S. K. (2019), ―Fundamental principles of froth floatation‖, SME Mining Engineering Hand book (P. Darling, ed), Littleton, CO, SME, Vol. 2, Pp1517-1531

Keeling JL, Raven MD and Gates WP 2000. Geology and characterization of two hydrothermal nontronites from weathered metamorphic rocks at Uley graphite mine, *South Australia. Clays and Clay Minerals* 48:537–548.

Keeling, J.L., (2017), Graphite; Properties, Uses and South Australian Resources. *MESA Journal 84,* 2017-issue 3

Lagaly, G. (2006) Colloid clay science. In: Handbook of Clay Science (F. Bergaya, B.K.G. Theng & G. Lagaly, editors). Developments in Clay Science, 1. *Elsevier, Amsterdam*, pp. 141– 245.

Lar, U.A. (2014), Project: Development and Utilization of Mineral Resources in Nigeria. Solid Minerals Sector and Inclusive Green Growth Strategy, doi: 10.13140/RG.2.1.1481.9365

Laird, D.A. (2006) Influence of layer charge on swelling of smectites. *Applied Clay Science*, 34, 74–87

Lee WE and Zhang S 2004. Direct and indirect slag corrosion of oxide and oxide-C refractories. Proceedings, VII International Conference on Molten Slags, Fluxes & Salts, Symposia Series S36. *The South African Institute of Mining and Metallurgy, Johannesburg*, pp. 309–319

Lee Sang-Min, Kang Dong-Su and Roh Jea-Seung. (2015), Bulk Graphite: Materials and Manufacturing Process. *Korean Carbon Society*. Vol. 16 Issue, pp. 135-146

Louppe, D., Oteng-Amoako, A.A., and Brink, M. (2008), Timbers1. Prota.Plant Resources of Tropical Africa, 7(1), http:// books.google.fr/book?id=-nw-mZQ0kcEC

Luque FJ, Ortega L, Barrenechea JF, Millward D, Beyssac O and Huizenga J-M 2009. Deposition of highly crystalline graphite from moderate-temperature fluids. Geology 37:275–278.

Lyckham, P.F. & Rossi, S. (1999) The colloidal and rheological properties of bentonite suspensions. Advances in Colloid and Interface Science, 82, 43 2 92.

Manfred, S. (2002). Pen or Pencil. US Patent No. 6409407B1, issued Jun. 25, 2002

Martin Vivaldi, J.L. & Robertson, R.H.S. (1971) Palygorskite and sepiolite (Hormites). In: Electron Optical Investigation of Clays (J.A. Gard, editor). *Mineralogical Society, London*, pp. 255–276

MacEwan, D.A.C. & Wilson, M.J. (1984) Interlayer and intercalation complexes of clay minerals. In: Crystal Structures of Clay Minerals and their X-ray Identification (G.W. Brindley & G. Brown, editors). *Mineralogical Society, London*, pp. 197

Mortland, M.M. (1970) Clay-organic complexes and interactions. Advances in Agronomy, 23, 75– 117.

Moore J. J. (1990): *Chemical Metallurgy*, Buttworth – Heinemann

Mitchell CJ 1993. Industrial Minerals Laboratory manual: Flake graphite, Technical Report WG/92/30. British Geological Survey, Keyworth, Nottingham.

Muhammed, A.M., El-Nafaty, U.A., Bugaje, I.M. (2014) Characterization of Graphite from Sama- Borkono, Bauchi State. *International Journal of Recent Development in Engineering and technology.*

Mukherjee S. (2013) Use of Clays as Drilling Fluids and Filters. In: *The Science of Clays . Springer, Dordrecht*. http://doi.org/10.1007/978-98-007-6683-9_11

Murray H.H. (2007) Applied Clay Mineralogy. Developments in Clay Science, 2. Elsevier, Amsterdam, 180 pp

Nwoke, M.A.U., Uwadiale, G.G.O.O., and Kollere, M.A., (1997), Floatation of low-grade Birnin-Gwari and Alawa Graphite, Nigeria. *Mining Metallurgy and Exploration*, 14, 54-56(1997). https://doi.org/10.1007/BF03402760

Orwa, C., Mutua, A., Kindt, R., Jamnadas, R., and Anthony, S. (2009), Agroforestree Database: a tree reference and Selection guide version 4.0 World Agroforestry Centre, Kenya.

Osasona, B., Alabi, O.O., Aramide, F.O., Akinyele, S.O., (2019), “The Grindability of Ningi Graphite Ore in Nigeria.” *Journal of Scientific and Engineering Research*, 2019,6(7):195-200

Parvinzadeh, M., Moradin, S., Rashidi A. & Yazdanshenas, M. E. (2010). Ultrasonic assisted finishing of cotton with nonionic softener. Polym. *Plast. Technol*. Eng. 49, 874-884

Peng, W., Qiu, Y., Zhang, L., Song, S., and Guan, J. (2017), Increasing the Fine Flaky Graphite Recovery in Floatation Via a Combined Multiple Treatments Technique of Middlings. *Minerals*, 2017, 7(11), 208; https://doi.org/10.3390/min7110208

Pruett, R.J. & Pickering, S.M. Jr. (2006) Clays. Kaolin. In: Industrial Minerals and Rocks, 7th edition (J. Elzea Kogel et al., editors). *Society of Mining, Metallurgy and Exploration, Littleton Colorado, USA*, pp. 383– 399

Rao, K.S. (2013). Strategic use of soil in war operations: the role of dispersion flocculation thixtrophy and plasticity of clay. *Defence Sci. J.*, 1(2), 192-204.

Raw Materials Research and Development Council (2010). Non-Metallic Mineral Endowment in Nigeria.

RMRDC. (2010), Non-Metallic Mineral Endowments in Nigeria; online edition (Accessed February 2014-02-16, 10:00 pm)

Ritter, S. (2001). Pencils & Pencil Lead. American Chemical Society. The History of the Pencil".University of Illinois at Urbana–Champaign."Module 6: Media for 2-D Art"(PDF). Saylor.org. Retrieved 2 April 2012.

Roskill Information Services, Ltd., 2015, National and Synthetics graphites- Global industry markets and Outlook, 8th ed.: London, Roskill Information Services Ltd., 413p.

Saba, S., Delage, P., Lenoir, N., Cui, Y. J., Tang, A. M. & Barnichon, J. D. (2014). *Further insight into the microstructure of compacted bentonite–sand mixture*. Eng. Geol., 168, 141-148.

Scott, P.W. (1990a) Brightness and Colour Measurement. CEC/ASEAN training course on assessment procedures for clays and ceramic ra

Schodde R. 2016. What to look for when making a graghite investment, presentation for battery metals summit, November 2016, London MinEx consulting, viewed July 2017, <http://www.minexconsulting.com/publications/R%20schodde%20-%20Graphite%20-%20 Battery%20summit%20FINAL%20NOV%202016.pdf>.

Slodkevich, V.V., (2009); Graphite paramorphs after diamond. International Geology Reviews 25, 497–514.

Sousa, M. C., and Butchanan, W. J. (2000), "Observational Models of Graphite Pencil Materials." *Models of Pencil Materials*, Vol. 18(1999)

Spencer R and Hill L 2016. A flake's change in cell: quantifying graphite demand, Canaccord Genecity Speciality Minerals and Metals and reports Volt Resources, viewed July 2017, <http://voltresources.com/wp/wp/wp-content/uploads/2016/12/canaciod.pdf>.

Stein V and Aneziris CG 2014. Low-carbon carbon-bonded alumina refractories for functional components in steel technology. *Journal of Ceramic Science and Technology* 5:115–124

Taylor, Harold A. (2005). Graphite. Industrial Minerals and Rocks (7th edition.). Littleton, CO:AIME- Society of Mining Engineers. ISBN 0-87335-233-5.

Tagiri, M., (2007). A measurement of the graphitizing-degree by the X-ray powder diffractometer. *Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists* 76, 345–352

Terrones, M., Botello-Méndez, A.R., Campos-Delgado, J., López-Urías, F., Vega-Cantú, Y.I., Rodríguez-Macías, F.J., Elías, A.L., Muñoz-Sandoval, E., Cano-Márquez, A.G., Charlier, J.C., and Terrones, H. (2010). Graphene and graphite nanoribbons: morphology, properties synthesis,defectsand applications. *Nano Today*, 5,351. http://dx.doi.org/10.1016/j.nantod.2010.06.010

Uddin, F. (2008). Clays, Nano-clays, and Montmorillonite Minerals. Metall. *Mater. Trans*. A. 39A, 2804-2814.

United State Geological Survey, (2009). Graphite Statistics and Information. USGS. Retrieved

2009-09-09

United States Geological survey (2017). Mineral commodity summaries 2017. United States geological survey, Reston Virginia.

United States Geological survey (2020). Mineral commodity summaries 2017. United States geological survey, Reston Virginia.

Wang GF 1989. Carbonaceous material in the Ryoke metamorphic rocks. *Lithos*22:303–316.

Wilhelm, H.A., Croset, B., and Medjahdi, G. (2007). Proportion and dispersion of rhombohedral sequences in the hexagonal structure of graphite powders. *Carbon*, 45, 2356. http://dx.doi.org/10.1016/j.carbon.2007.07.010.

Wills, B. A. and Napier-Munn, T. (2006): *Mineral Processing Technology-An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery*, Seventh Edition, Amsterdam: Elsevier Science and Technology Books, P450

Xiaowei, L., Jean-Charles, R., and Suyuan,Y. (2004). Effect of temperature on graphite oxidation behavior. Nucl Eng Des, 227, 273. http://dx.doi.org/10.1016/j.nucengdes.2003.11.004

Yoshio M, Wang H, Fukuda K, Umeno T, Abe T and Ogumi Z 2004. Improvement of natural graphite as a lithium-ion battery anode material, from raw flake to carbon-coated sphere. *Journal of Materials Chemistry* 14:1,754–1,758

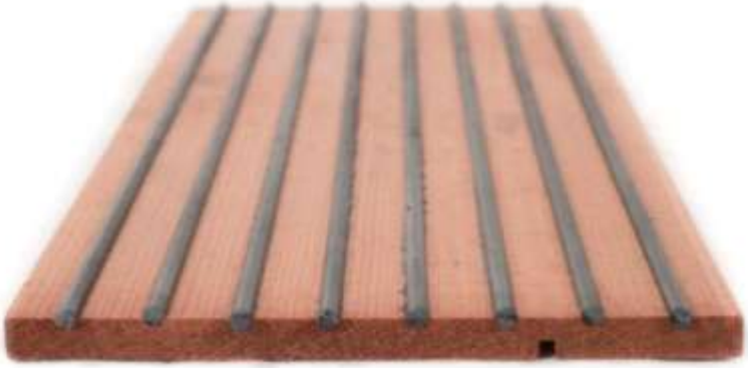
APPENDICES

Appendix I: HB Pencils (https://blog.pencils.com)

Appendix II:Pencil leads(https://blog.pencils.com)

Appendix III: pencil block(https://blog.pencils.com)

Appendix IV: Slats (https://blog.pencils.com)

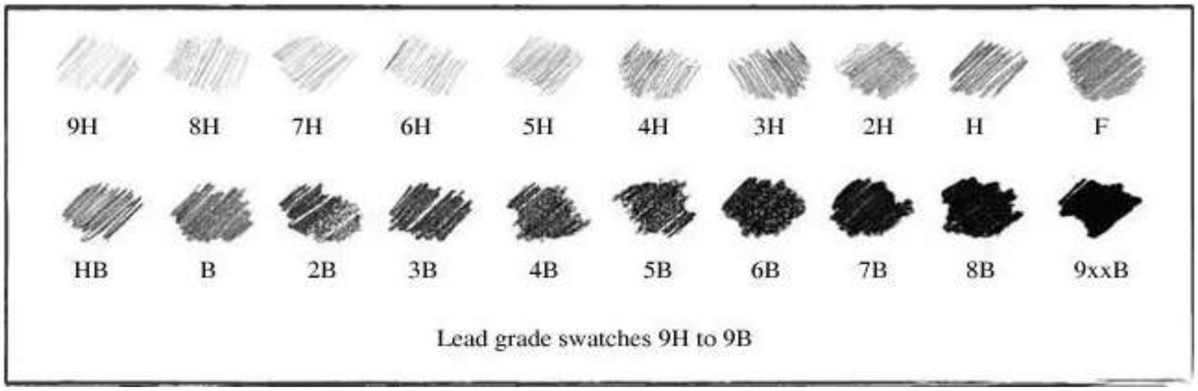


Appendix V: Pencil leads inside grooves(https://blog.pencils.com)

Appendix VI: Slats sandwich(https://blog.pencils.com)

Appendix VII: machined sandwiches(https://blog.pencils.com)

Appendix VIII:different pencil grades (Wright, 2018)



Appendix IX: variation of pencil lead hardness with clay content

s