

**BENEFICIATION OF BAUCHI GRAPHITE FOR CRUCIBLE PRODUCTION.**

**NWOBI, BRIDGET EGBI**

**DEPARTMENT OF CHEMICAL ENGINEERING  
FACULTY OF ENGINEERING  
AHMADU BELLO UNIVERSITY  
ZARIA**

**OCTOBER, 2006**

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AHMADU BELLO UNIVERSITY  
ZARIA**

**OCTOBER, 2006**

## CERTIFICATION

This project report entitled **BENEFICIATION OF BAUCHI GRAPHITE FOR CRUCIBLE PRODUCTION** by **NWOBI, BRIDGET EGBI** meets the regulations governing the award of the degree of M.Sc (Chemical Engineering) of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

\_\_\_\_\_  
Dr. A.S. Ahmed  
Chairman, Supervisory Committee

Date: \_\_\_\_\_

\_\_\_\_\_  
Dr. B.O. Aderemi  
Member, Supervisory Committee

Date: \_\_\_\_\_

\_\_\_\_\_  
Dr. B.O. Aderemi  
Head of Department

Date: \_\_\_\_\_

\_\_\_\_\_  
Prof. J.U.Umoh  
Dean, Postgraduate School

Date: \_\_\_\_\_

## DECLARATION

I declare that the work in the thesis entitled “BENEFICIATION OF BAUCHI GRAPHITE FOR CRUCIBLE PRODUCTION” has been performed by me in the Department of Chemical Engineering under the supervision of Drs. A.S. Ahmed and B.O. Aderemi. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any university.

NWOBI, BRIDGET EGBI

DATE: \_\_\_\_\_

## **DEDICATION**

This project is dedicated to my lovely husband (Israel Nwobi) and to my children (Harrison, Chibuike, Obi-Eze, Divine Favour and Junior Israel).

## ACKNOWLEDGEMENT

All glory, honour, adoration and praise be to God and my Lord Jesus Christ for His mercy, favour, love and kindness to me. Indeed, He has been good to me, and has been the source of my inspiration. His guidance, protection and favour has brought me thus far especially to the completion of this work.

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I will remain grateful to my supervisors Dr. A.S. Ahmed and Dr. B.O. Aderemi for their support, encouragement, fatherly advice and listening ears. May the Almighty God reward you all.

To my darling husband(Isreal Nwobi), I am very grateful for your support (morally and financially) and understanding you gave to me throughout this M.Sc. work. May the Almighty God grant you your heart desires. To my children (Harrison, Chibuike, Obi-Eze, Divine-Favour and Junior Israel), I say thanks for your understanding. I am sorry for those times you needed me and I was not there. I hope you will understand someday. To my parent, I lack what to say, May the Almighty God spare your lives and to keep you all in good health. To my other family members, I say thanks for being there for me. Uwane, Ruth and David. I say special thanks to you for taking care of my family when I am not there.

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Finally, thanks to my classmates (for the encouragement you gave to me) and to the staff of Pilot Plant Department NARICT, Zaria.

## Abstract

Crucibles are manufactured from naturally occurring substance in the earth crust – clay, quartzite, chromate, bauxite, graphite etc. All these materials do not occur in their pure form, hence needs some form of treatment before their usage in manufacturing.

In this study, the graphite from Bauchi State of Nigeria was beneficiated and characterized. The optimum pulp condition for the floatation using froth floatation method was found to be at, 0.3mls of kerosene, 0.5 mls of turpentine and 0.3 mls of 25%  $\text{Na}_2\text{CO}_3$  in 50g of graphite ore with 300 mls of water. It was also found that, the agitation time required for optimum recovery before and after addition of the reagent was 10 minutes and 5 minutes respectively.

The carbon content was found to be 82wt % for the beneficiated and 42wt% for the raw sample. The density of the beneficiated sample was found to be  $2,250 \text{ kg/m}^3$  which closely agrees with the literature value of  $2,260 \text{ kg/m}^3$ . The largest flake size was found to be about  $1000\mu\text{m}$ , which makes it a good material for crucible production.

30kg tar bonded crucible were formed using data from laboratory results earlier carried out. But every effort made to fire the crucible failed. Reasons for the failure could not be ascertained. The use of clay pots as substitute for the conventional saggars in the firing could be responsible due to the low gas permeability of the pots.



## Abbreviation and Symbols

C	-	Constant weight of dry sample (kg)
S	-	Weight of the sample suspended in water (kg)
W	-	Weight of the sample in air (kg)
P	-	Fraction of the particle size (%)
d	-	Average between the largest and smallest particle size in a particular fraction( $\mu\text{m}$ )
D	-	the largest particle size in a particular fraction( $\mu\text{m}$ )
n	-	Andreason parameter
wt	-	Weight (kg)
%	-	Percentage
kg	-	Kilogram
$\text{m}^3$	-	Meter cube
“	-	Inches
CBN	-	cubic boron nitride
$\pi$	-	Pie
POP	-	Plaster of Paris
DOS	-	Degree of saturation.
30kg crucible	-	A crucible that can carry 30kg of molten copper metal
Forex	-	Foreign exchange

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## CHAPTER ONE

### INTRODUCTION

Technological advancements have led to the development of a special class of refractories, which promotes effective and efficient operation of new processes in steel making with marked reduction in the consumption of refractories per ton of steel produced. Such refractories are called “Ceramic graphite refractory” products and they have excellent features for applications where resistance to thermal shock and basic slag at high temperatures is needed (Chesti, 1986). For these reasons, they are used in producing crucibles. These crucibles are high refractory, open mouth vessels made of graphite and ceramic materials.

Graphite is found naturally in the earth crust though it can also be manufactured artificially from petroleum coke using electrical furnace. Graphite is a crystalline and most stable form of carbon that occurs as mineral. It can be used in many ways because of its resistance to high temperature, resistance to corrosive chemicals and oxidants, and its non-wittedness. These qualities accounts for its effectiveness and high efficiency in graphite crucibles. In the US, it is used for steel making refractories and crucibles (Graffin, 1975). These account for about 70% consumption with the 30% remaining being used for lubricant, pencils, brake lining and batteries.

In Nigeria, graphite can be found in Birnin Gwari (Kaduna State), (2.78% - 4.37% graphite), Gayama Area of Taraba State, Maiyo Butale, Hossere Nuwa and Jauro Jalo Area of Adamawa State(20% graphite), Alawa Area of Niger State and in Duchin

Hai (Dutsen Haiyar) in Bauchi State (30% graphite) [Falconer et al (1923), GSN (1974), Jacques (1943)].

The Bauchi Graphite which is found to contain higher quantity of the graphite (30%) has not been well characterized, not to talk of its exploitation in crucible production.

A lot of works (unpublished) has been done here in the Department of Chemical Engineering Ahmadu Bello University, Zaria on production of crucible but in smaller sizes (laboratory scale) and thus there is the need to produce life size crucible using the results generated from the laboratory.

Aloa, (1999), Adefila (2000) and Olaniyan (2001) have produce crucibles using graphite from Gayama area. The crucibles produced were either clay or tar bonded. It was found that the tar bonded crucible did not require a lot of pressure to form it. It was also found that the tar bonded has lesser porosity which will eventually increase its resistance to slag attack, hence the use of tar as a binder in this work.

## **1.1 Statement of Problem**

The Bauchi Graphite which is found to contain high quantity of the graphite (30%) has not been well characterised. The last known information about it was by Jacques (1943). He reported that the graphite from Bauchi (Duchin Hai) is of higher quality than other graphite in Nigeria. In agreement with the Federal Government policies on been self reliant, it is imperatively important to characterize more properly our local raw materials and gear them towards product development purposes.

In Nigeria a lot of foundry activities are springing up which need the use of crucibles. Hence the Raw Material Research and Development Council deemed it fit to go into the research for the production of life size crucibles which led to this research work.

## **1.2 Justification**

A lot of Foreign exchange earnings (Forex) is being used annually to buy these crucibles because they are very important in the foundry industry. Furthermore, due to increase in foundry activities, there is an increase in demand for crucibles. Consequently, there is the need to produce it in Nigeria since we have the required raw materials (graphite, kaolin and petroleum coke) in desired quantity and quality.

Nigeria will be self reliant and we will be able to save our Foreign exchange, and provide employment for our people.

## **1.3 Scope**

The scope of this work includes: to beneficiate graphite using froth flotation method to get the best possible grade of graphite (graphite crucibles require high grade), determining the best particles size distribution, carbon content and density of raw and beneficiated samples. Also a 30kg graphite crucible was produced using a hydraulic press. And a clay pot was used for firing in place of a conventional saggar. The locally available kiln was used for the firing. Finally the microstructure of the crucible was examined.

## 1.4 Objectives

The objectives of this research work are:

- 1) To beneficiate the Bauchi graphite while preserving its aggregate form and size.
- 2) To characterize the raw and beneficiated Bauchi graphite.
- 3) To produce a life size graphite crucible (30kg) that can meet international standard using locally available materials (graphite, kaolin; coal tar as binder and silicon powder as additive), using hydraulic pressing method.

## CHAPTER TWO

### LITERATURE SURVEY

Graphite crucibles are high refractory, open-mouthed vessels made of graphite. They are used for melting cast iron, glass, various metals and alloys.

#### 2.1 Graphite

Graphite is a crystalline form of carbon with a hardness of 1 – 2 on Mohr's scale (Chesti, 1986). It is an excellent conductor of heat and electricity and melts at about 3,500°C. It is very stable up to temperature above 620°C above which it is combustible in the presence of oxygen.

##### 2.1.1 Occurrence

- i. Natural graphite occurs in three forms: [Cirkel, 1966].
  - (a) Disseminated crystals, found as lamellae in metamorphic marbles, gneisses and schists (flake grade). They are distributed through the body of the ore or in concentrated Lens shaped pockets. Carbon concentrations vary between 5% and 40%.

Flake graphite are removed by froth flotation. "As floated" graphite contains between 80% and 90% graphite.

- (b) Crystalline veins (fibrous or columnar), found often along pegmatite limestone contacts (lump grade ore). They are believed to originate from

crude oil deposits that through time, temperature and pressure have converted to graphite. Vein graphite fissures are typically between 1cm and 1m thick, and are typically > 90% pure.

- (c) Amorphous, (which in fact is microcrystalline) occurs in low grade metamorphic rocks such as slates and shale (lower grade). However, the term “amorphous” is a misnomer since the material is still crystalline. Amorphous graphite is found as minute particles in beds of mesomorphic rocks such as coal, slate or shale deposits.
- ii. Graphite can be produced artificially too. It is produced from petroleum coke using electrical furnaces. They tend to be of higher quality though not as crystalline as natural graphite.

### **2.1.2 Graphite in Nigeria**

It is known that graphite has been in use for decoration of houses in Nigeria [Falconer et al. 1923], but there is no record of its commercial production. Geological Survey of Nigeria [GSN, 1973] reported some deposit areas. The deposit occurs in Birnin Gwari in 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. Also graphite is found in Alawa area of Niger State.

#### *2.1.2.1 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 50km wide of schistosity 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 6.5km north of Birnin Gwari (old town), 90km NW of Kaduna. In hand specimens, the graphite is very fine grained and powdery.

#### *2.1.2.2 Graphite deposits in Adamawa State.*

“Minerals and Industry in Nigeria’ (1957) a publication of the Geological Survey of Nigeria, mentions the occurrence of graphite. Unfortunately no records are available concerning Hossere Nuwa, and Jauro Jalo occurrence but that of Maiyo Butale (08<sup>0</sup>00’20” N and 11<sup>0</sup> 59’ E) have been examined. The graphite at Hossere Nuwa (07<sup>0</sup> 51’ N and 11<sup>0</sup> 24’ 30” E) and Jauro Jalo (07<sup>0</sup> 37’30” N and 11<sup>0</sup> 08’ E) has 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 N60<sup>0</sup>W and interpreted as a shear zone by Ikejiaku.

### *2.1.2.3 Gayama graphite in Taraba State*

“Minerals and Industry in Nigeria’ (1957) a publication of the Geological Survey of Nigeria, mentions the occurrence of graphite in Gayama Area in Taraba State. Its occurrence is found at Gayama(07°47’N and 11°10’30’E)

### *2.1.2.4 Duchin Hai (Dutsen Haiyar) Bauchi State graphite*

Falconer and Raeburn (1923) first reported this locally, which was later, examined in more detail, trenched and described by Jacques (1943). The graphite occurs at approximately, 11°08’ N and 9° 41’ E on the west bank of the Delimi, (Bonga) River in Ningi L.G.A., and due ENE of Ningi town which is 90km NNW of Bauchi.

Presently, an old pit of 24m long, 3.5m wide and 2m deep which is partially filled with debris exist. There are also three additional trenches dug to the north and south of the old pit. The graphite occurs in a schistose band striking N10°W, dipping 60° to 80° eastward and can be followed for about 80m along strike. Towards the north end, the graphite quartz-Ferruginous band narrows to less than 1m and is more ferruginous, while to the south it widens to 4m or more and contains higher graphite content up to 30%. This graphite is known to occur as flakes between quartz crystals. Since the content is high, it is then advantageous to use this sample for this study.

### **2.1.4 Beneficiation of graphite**

Graphite ore do not occur pure in nature. They usually occur with some impurities such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, clay, oxide of metals etc. It is then important to beneficiate the graphite before its usage. To beneficiate the ore, there are four

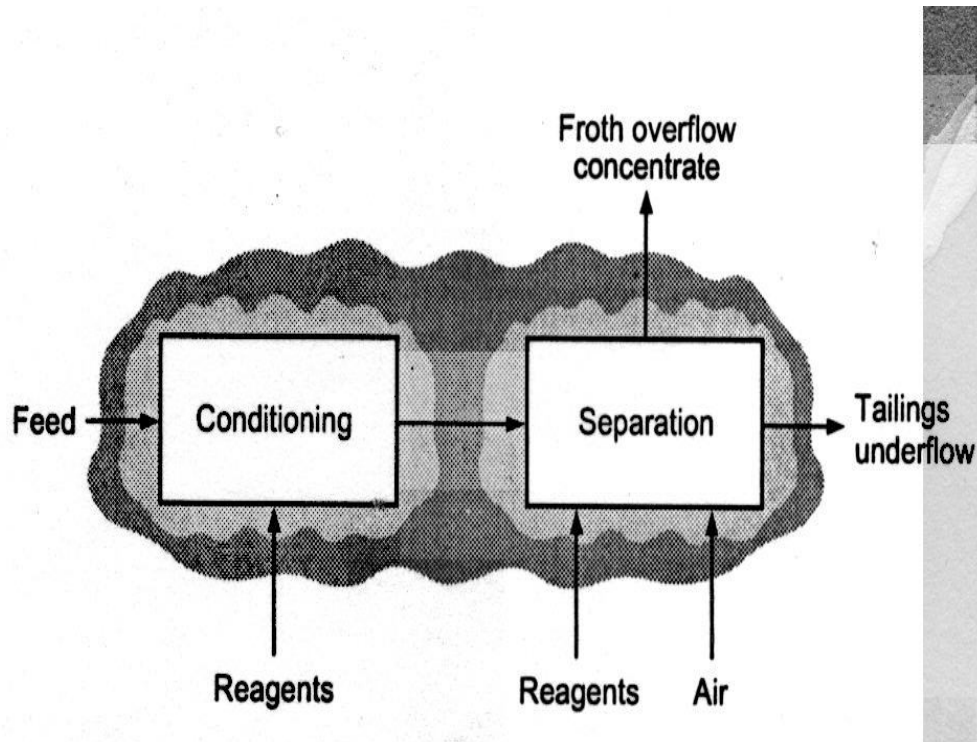
methods of beneficiation: (a) froth flotation (b) magnetic separation (c) washing (d) chemical leaching.

Froth floatation is mostly use for the beneficiation of graphite ore. In case where very high purity is required a combination of beneficiation process is used.

#### *2.1.4.1 Floatation*

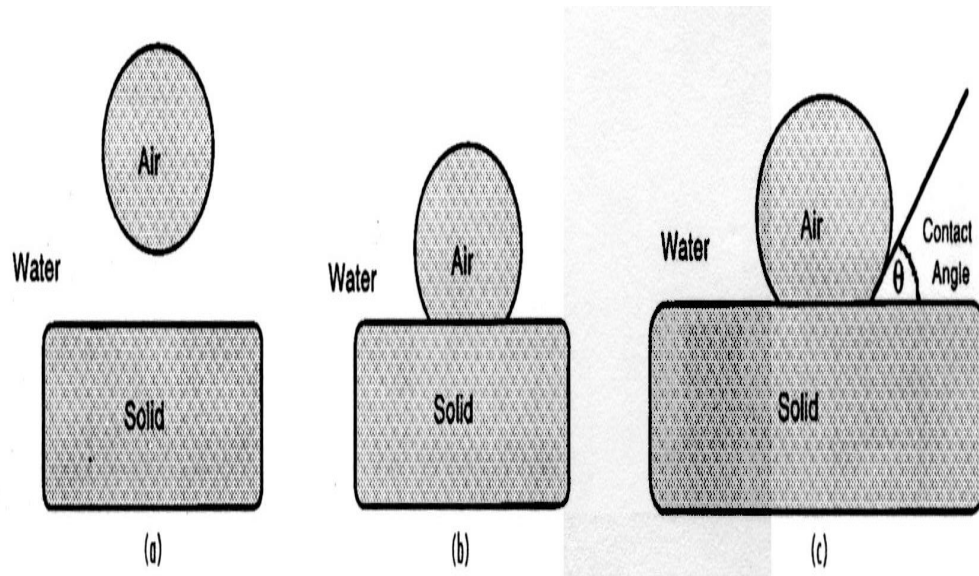
Mixed liberated particles can be separated from each other by floatation process operates. If there are sufficient difference in their wettability. The floatation process operates by preparing a water suspension of a mixture of relatively fine-sized particles (smaller than 150 $\mu\text{m}$ ) and by contacting the suspension with a swarm of air bubbles of air in a suitably designed process vessel. Particles that are readily wetted by water (hydrophilic) tend to remain in suspension, and those particles not wetted by water (hydrophobic) tend to be attached to air bubbles, levitate (float) to the top of the process vessel, and collect in a froth layer. Thus differences in the surface chemical properties of the solids are the basis of separation by flotation.

The floatation process is most widely used in the mineral process industry to concentrate mineral values in the ores. Unit operation of floatation is based on two major steps (1) conditioning and (2) separation as is shown in Figure 2.1.

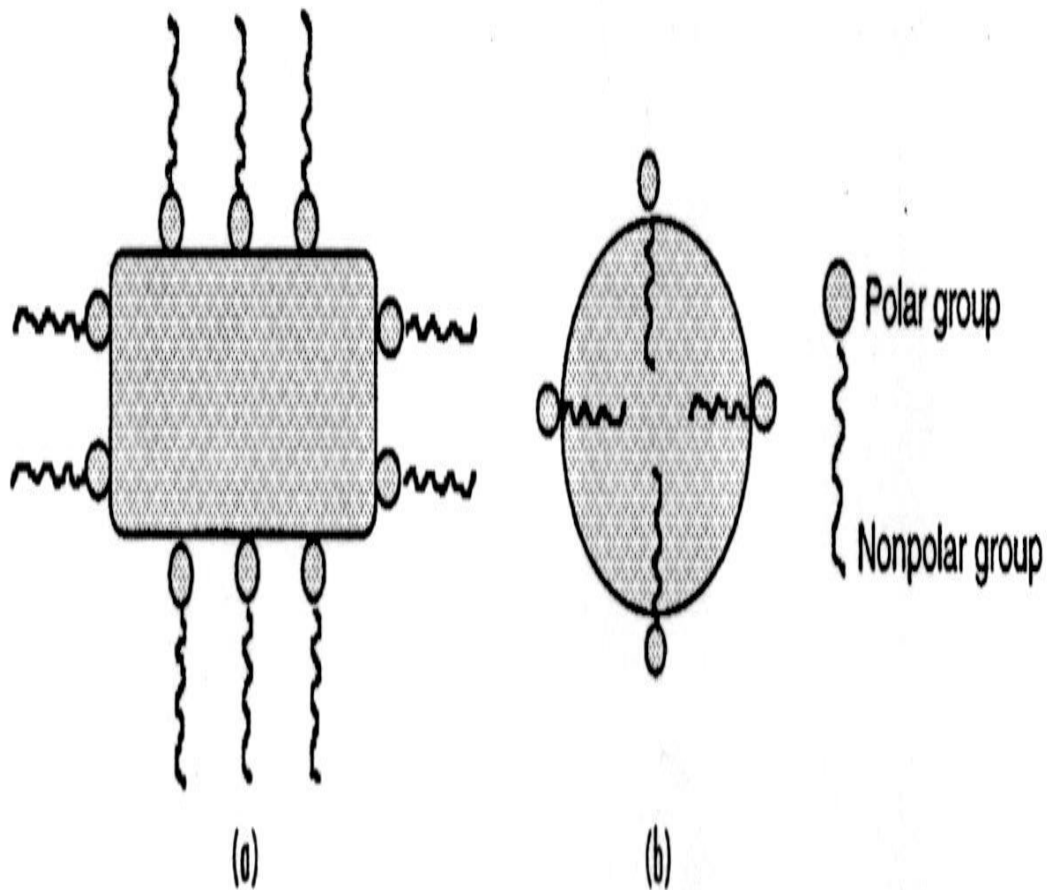


**Figure 2.1: Basic Steps in a Flotation System**

During the first step, the slurry or the pulp, consisting of particles to be separated, the particle size of which is already properly adjusted, is fed to the conditioning unit, to which the necessary floatation reagents are added. The main purpose of the conditioning step is to create physical – chemical conditions for achieving appropriate selectivity between particle species that are to be separated. The second step is then intended to generate and introduce air bubbles into the process vessel – for contacting them with particulate species so as to affect their separation by floatation. Particles attached to the air bubbles are in most applications removed from the process vessel as froth. The process is shown in Figure 2.2 and Figure 2.3.



**Figure 2.2: Schematic Representation of Air Bubble Water-Solid Particle System; (a) Before, (b) After Particle-Bubble Attachment, and (c) Equilibrium Force Balance.**



**Figure 2.3: Schematic of (a) Collector Adsorption at the Particle Water Interface and (b) Action of the Frothier**

### 21.3.2 Flotation reagents:

Three types of flotation reagents are used during froth flotation process.

(a) Collectors: These are surface – active agents that are added to the flotation pulp, where they adsorb selectively on the surface of the particles and render them hydrophobic. Examples of collectors are fuel oil (kerosene), fatty acids, long-chain sulphates, sulphonates and amines, xanthates and dithiophosphates. Dosage requirements for collectors depend on the mechanisms by which they interact with the particle surface, but just enough is needed to form a monomolecular layer.

(b) Frothiers: These are also surface – active agents added to the flotation pulp primarily to stabilize the air bubbles for effective particle-bubble attachment carry over of particle – laden bubbles to the froth, and removal of the froth. Commonly used frothiers and pine oil, greasily acid, polypropylene glycol. short chain alcohols and 5-to 8- carbon aliphatic alcohols.

(c) Modifiers: Flootation modifiers include several classes of chemicals. The modifier includes activators, pH regulators, depressants, dispersants and flocculants. The pH regulators includes lime, caustic soda, soda ash and sulphuric acid are used to control or adjust pH, a very critical factor in many flotation separations.

#### *2.1.3.3 Flootation equipment:*

There are different types of floatation equipment. Each of them has its advantages and limitations. For a choice to be made it is necessary to contact the manufacture. Below is a diagram of how the D – R Denver froth floatation equipment works. Figure 2.4 and 2.5 are the schematic diagram of the Denver equipment.

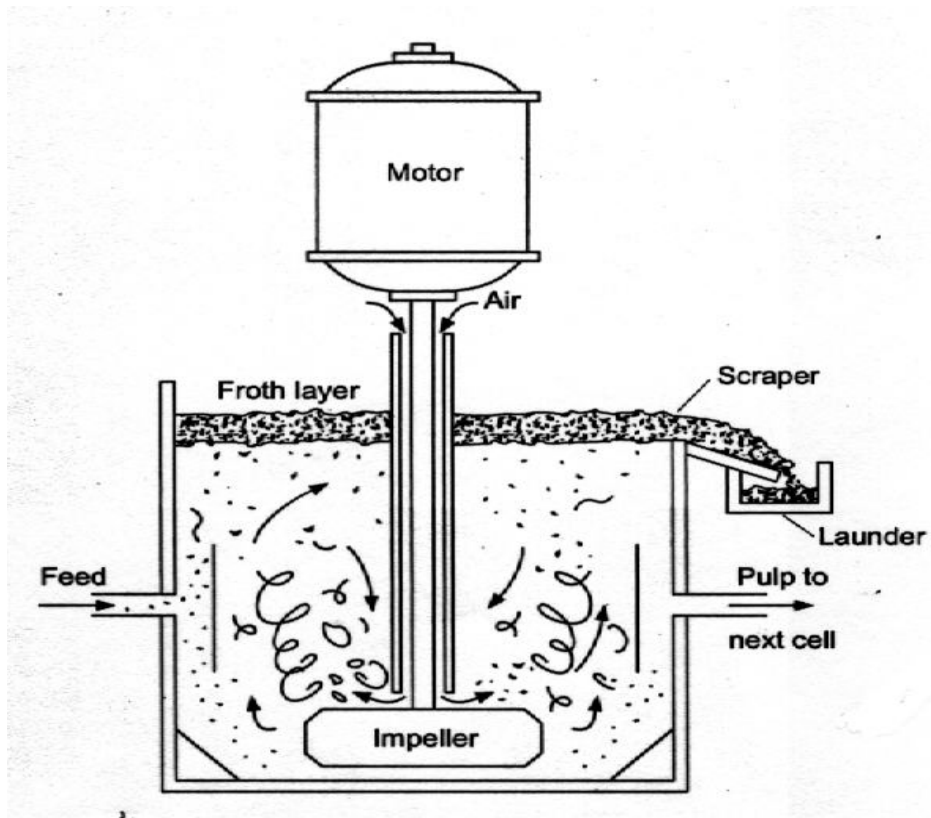
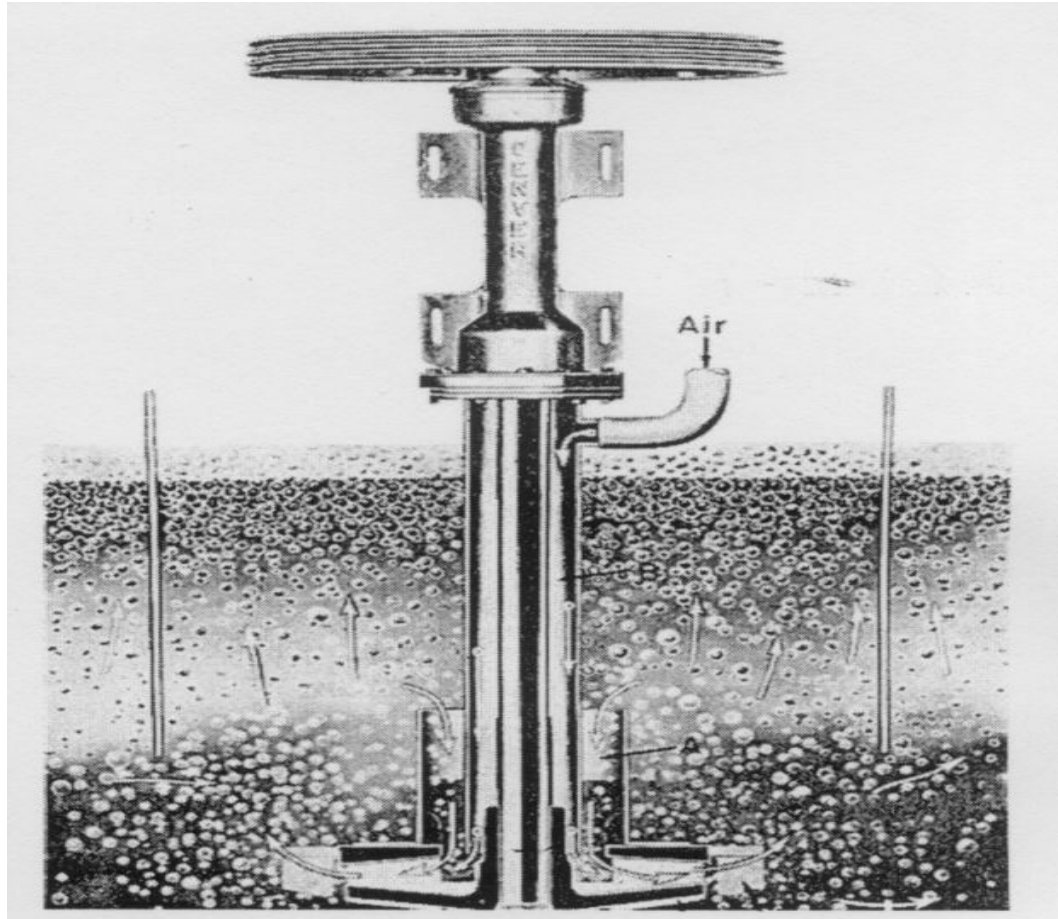


Figure 2.4: Schematic of a Mechanical Flotation Cell.





**Figure 2.5: D-R Denver Flotation Machine**

## 2.2 Crucibles

Crucibles are open mouthed vessels used for melting various metal and alloys. Industries dealing with treatment of ores and other materials for the manufacture of metallurgical, chemical and ceramic products need high temperature, hence to treat such materials, materials that can withstand such operating temperature and other working conditions such as corrosiveness, erosiveness and load conditions, are needed. Crucibles are class of materials that can withstand high temperature (say  $1000^{\circ}\text{C}$ ), resist the action

of corrosive liquids and dust-laden currents of hot gas etc. There are different types of crucible depending on the raw material used for its production. These materials also determine the property it will have. Properties of good crucibles include:

- (a) High refractoriness – this means resistance to fusion and softening at the working temperature.
- (b) High resistance to thermal fatigue – ability to withstand sudden change in temperature.
- (c) Resistance to abrasion – capacity to resist the rubbing action of the material coming in contact with it.
- (d) Resistance to corrosion – inertness to the chemical action of molten metal, slag or gases that it comes in contact with.
- (e) High refractoriness under load – its ability to resist crack, crumble or deformation under the action of pressure and temperature.
- (f) Low porosity and permeability – It should have the ability of not allowing gases and liquids to pass through it.
- (h) High thermal conductivity – ability to promote heat transfer as in recuperative type of furnaces.
- (i) Low coefficient of thermal expansion and contraction – it should exhibit the least structural change on heating or cooling without disintegration.

- (j) Price: The price of material used per ton of steel produced is very important. A material with longer life cycle is very important. For a material with high price and long life cycle might be cheaper than a material with low price which will crumb fast.

However, all these properties cannot be found in any one material, hence, depending on the usage, the material that will fit such operation is chosen specifically for that purpose.

### **2.2.1 Properties of graphite crucible**

The properties mentioned above can be determined, and quantified.

#### *2.2.1.1 Refractoriness*

This is the measure of the fusibility of a material and it shows the temperature at which the material softens. The fusion point of some pure materials is shown in Table 2.1.

**Table 2.1: Important Refractory Materials and Their Fusion Temperature**

<b>Compound</b>		<b>Fusion Temperature °C</b>
Silica	(SiO <sub>2</sub> )	1715
Mullite	(3Al <sub>2</sub> O <sub>3</sub> ,2SiO <sub>2</sub> )	1810
Sillimanite	(Al <sub>2</sub> O <sub>3</sub> ,SiO <sub>2</sub> )	1816
Titania	(TiO <sub>2</sub> )	1850
Alumina	(Al <sub>2</sub> O <sub>3</sub> )	2050
Spinel	(MgO,Al <sub>2</sub> O <sub>3</sub> )	2130
Carborundum	(SiC)	Solid at 2240
Chromium Oxide	(Cr <sub>2</sub> O <sub>3</sub> )	2275
Beryllia	(BeO)	2530
Lime	(CaO)	2570
Zirconia	(ZrO <sub>2</sub> )	2677
Magnesia	(MgO)	2800
Thoria	(ThO <sub>2</sub> )	Solid at 3000
Carbon	(C)	Solid at 3600

Courtesy: Chesti (1986).

In the manufacture of refractories, it is important to know that when other substances are added to a material, it lowers the fusion temperature. The effect of the added material depends on:

- i) Amount of impurities present
- ii) The fusion temperature.

- iii) The ability of the lowest fusion constituent to dissolve the material of higher fusion point at relatively low temperature.

Even though the addition of other substance reduces the fusion temperature, it is still added because it serves as a binder in the production of refractories. This material forms a glassy phase and hence will fuse the material together.

The refractoriness can be expressed using the Pyrometric Cone Equivalent (P.C.E.). This can be obtained by comparing the softening of a test pyramid cone with that of standard pyramid cone of known fusion temperature by heating them under similar condition. From Table 1, it is seen that graphite (carbon) is still solid at 3600°C, which means that the material is good to be used for foundry activities since they can withstand high temperature. In foundry, the molten metals temperature is about 1600°C, hence the crucible needed should be able to withstand higher temperature without failing.

#### *2.2.1.2 Resistance to Thermal Fatigue:*

This is the ability of a crucible to withstand sudden changes in temperature. A crucible that is subjected to alternate cycle of heating and cooling must not spill or crack or crumble to pieces so that the substance in it will not be lost. Crucibles made of materials with low thermal coefficient of expansion and coarse tenures have increased resistance to sudden change in temperature. When manufacturing a crucible and the raw material is not uniformly mixed, fracture can occur because the product will then have non-uniform coefficient of thermal expansion. This can also occur as a result of structural change during operation. This defect can be controlled by mixing properly and burning the crucible at a temperature higher than the service temperature so as to prevent

slag penetrating into the pores. Fracture can also be caused by uneven heating and cooling during the burning of the refractory material. Hence it is necessary to heat and cool gradually while producing the crucible. Also long heating of the crucible material at high temperature brings about complete material inversion and thus the finished crucibles have a high resistance to thermal fatigue.

#### *2.2.1.3 Resistance to Abrasion*

Abrasion occurs when a material comes across a moving charge, which rubs against it and subjects it to wear. In case where there is abrasion, it is preferable to use a dense, fine-grained and wear resistant refractory lining. To achieve these in graphite crucibles, the different particle sizes of both the clay and graphite is expected to be mixed in a specified proportion using the Andreason equation (Chesti 1986) to get the required mixing ratio.

#### *2.2.1.4 Resistance to Corrosion*

This is one of the most important qualities of crucible because crucible comes in contact with slag. The resistance of the refractories depends on the nature and composition of the slag, the temperature and also whether the slag is stationary or it is moving or is it carried as fine particles or by the fume or gases. If the slag is capable of forming new compounds with the crucible, then there will be slag action. This is because the slag will dissolve some of the refractories and it will change its composition and hence the melting temperature will be altered. Graphite crucibles are one of the best to be used because they are neutral to slag and hence can not be corroded. (Jahanshahi et al 2000).

#### *2.2.1.5 Refractoriness under Load:*

This is the ability of a refractory to resist crack, crumble or deformation under the action of pressure (load) and temperature. It is the softening temperature at which a test specimen breaks down when a load of 2.00kg per square centimetre is applied. The failure of a refractory is influenced by the time of its exposure to heat and load.

#### *2.2.1.6 Porosity and Permeability:*

Porosity is the percentage relationship between the volume of the pore space and the total volume of the refractory. While permeability is a measure of the rate at which a fluid can pass through a porous material, the porosity of a material determines its permeability. The higher the porosity, the higher the permeability, the lower the strength, the less heat conducted and the less sensitive to fluctuation of temperature.

The pores in a material can either be open or closed. These two types of pores influence the density. The density can either be bulk which is affected by the open pores or true density which is affected by both the closed and open pore space. Porosity can be either apparent or true porosity. To increase the bulk density it is needed to close the open pore spaces. Coal tar can be used to block this pore spaces. Also a less porous crucible is better because, that will reduce the space for slag to enter, and this will prevent it from been attacked by chemical (slag) and its rate of breakage will be reduced. (Chesti 1986)

$$\text{Bulkdensity} = \frac{D}{W - S}$$

$$\text{Apparent Specific Gravity} = \frac{D}{D - S}$$

$$\text{Apparent Porosity} = \frac{W - D}{W - S} \times 100$$

Where  $D$  = constant weight of the dry sample

$S$  = weight of the specimen suspended by water

$W$  = weight of the specimen in air

Porosity is the percentage relationship between the volume of the open and close pore space, and the total volume of the sample. (Jahanshahi et al 2002.)

### 2.2.1.7 Thermal conductivity

This is the ability for a material to conduct heat. The thermal conductivity of a material decreases with an increase in porosity because the pores create air spaces which are bad conductors of heat.

Table II show the thermal conductivities of some refractory materials.

**Table 2.2: Thermal Conductivities of Some Refractory Materials**

Material	Room Temperature e.g.s. Unit			
	300 <sup>0</sup> C	700 <sup>0</sup> C	1100 <sup>0</sup> C	
Silica	-	0.003	0.004	0.005
Fireclay	0.0023	0.002	0.002	0.003
Sillimanite	-	0.003	0.004	0.004
Magnesiae	-	0.011	0.008	0.007
Chrome	-	0.004	0.004	0.005
Chrome Magnesite	-	0.005	0.005	0.004
Insulating Firebricks	0.0007	0.0006	0.0008	0.001
Kieselguhr	0.0001	0.0003	0.0004	-
Asbestors	0.00008	0.00001	0.001	-
Slag Wood	-	0.0001	0.0001	-
Carbon	0.1	-	0.005	0.008
Graphite	-	0.21	0.12	0.08
Carbonrudum	-	-	-	0.02

\*Courtesy: Chesti (1986).



From Table 2.2, it is seen that graphite has higher thermal conductivity than the other materials. Hence, when molten metal is put in it, it will conduct the heat fast. But the presence of clay which has low conductivity will reduce the heat conducted and therefore, the crucible produced with both materials will be easy to handle even when hot molten metal is poured into it.

#### *2.2.1.8 Crushing Strength*

Refractories should be able to withstand the weight of load placed on them. Dense and fine grained refractories generally have better crushing strength than porous and coarse grain ones. To get a good crucible with high crushing strength, it is required that a mixture of fine and coarse sizes is used, using the Anderson equation to get the best proportion for each size.

#### *2.2.1.9 Resistance to Erosion:*

This is done when molten metal or gas carrying dust and slag particles strikes against a refractory lining, resulting in the chipping off of particles from it. Therefore, it is important to choose carefully the particle sizes of the raw materials so as to be able to withstand such a condition so as to resist the erosive effect of the medium.

#### *2.2.1.10 Price*

The cost of a material is very important. There are other precious metals that could be used for making crucibles. Metals such as tungsten but it is very expensive hence graphite crucible are chosen since they are cheaper and still it can do the same work like those metals.

The cost of a refractory material is very important when selecting. It should be as low as possible i.e. the cost per unit weight of the material should be considered more than the initial cost. A costlier refractory material, which is having a longer life span, may be cheaper at the long run than an initially cheap one. The cost also is dependent on the quality of work it is being used for. In the final analysis it is the over-all cost of the refractory that determines its use for a particular installation.

### **2.2.2 Classification of crucibles**

There exist different types of crucibles ([www.zircar.com](http://www.zircar.com)).

#### *2.2.2.1 Graphite Crucibles*

They are refractory crucibles of high thermal shock resistance with little tendency to oxidize their contents. They are highly resistant to chemicals except to oxidation. They can be otherwise called refractory carbonaceous. The crucible (graphite crucibles) usually contains 30 – 50% flake natural graphite. Binders such as clay, plastic clay, tar or pitch and silicon powder (2%) are usually added in weight percent to give strength before firing and prevent further oxidation respectively (Harold 1986)

#### *2.2.2.2 Alumina Crucibles*

They are characterized with very high refractoriness to boiling or fused alkaline. They also exhibit high thermal conductivity resistance to acid and basic slag. They can be prepared from the following raw materials:

- Bauxite diasporite plus refractory fireclay

- Sintered corundum and binder
- Fused alumina and binder
- Mixture of the three above

#### *2.2.2.3 Graphite/Silicon Carbide Crucibles*

They are carbonaceous in nature. The raw materials used in manufacturing include graphite, silicon carbide and tar.

#### *2.2.2.4 Silicon Carbide Crucibles*

These are characterized with high thermal conductivity and therefore fuel saving, high resistance to thermal shock and spilling, clean pouring but stain some contents such as glass. The raw materials include silicon carbide, bond clay or other binders.

#### *2.2.2.5 Magnesite Crucibles*

These are used for melting of platinum and other refractory materials and in electric furnaces. Raw materials used include dead burnt magnetite (fired above 1550<sup>0</sup>C), binders such as caustic magnesite and magnesium chloride.

#### *2.2.2.6 Sillimanite Crucibles*

It is being used for melting glasses for optical and experimental purposes. The body type is aluminosilicate which gives sillimanite. Raw materials used include ball clay, China clay, sillimanite minerals and alumina. They have better resistance to acid than to basic slag.

## **2.3 Shapes of Crucible**

Crucibles are available in a number of designs including barrel-shaped, conical, cylindrical, high form, skull melting, tongue and groove or furnace liners and wide form. [www.zircar crucible.com]

### **2.3.1 Barrel crucible**

Barrel crucibles have an opening with a top outer diameter that is essentially the same as or only slightly smaller than the base or bottom outer diameter. The side walls bulge out producing a barrel shaped crucible.

### **2.3.2 Conical or tapered crucible**

This type of crucibles has an opening with a top outer diameter that tapers down to smaller base or bottom diameter. The side walls are straight side.

### **2.3.3 Cylindrical or straight walled crucibles**

They have an opening with a top outer diameter that is essentially the same as or only slightly smaller than the base or bottom outer diameter. The side walls are straight sided without any bulging out.

### **2.3.4 Skull melting crucible or melting hearths**

This type of crucible has water or salt cooled copper shell that maintains an unmelted skin or skull of metal. The unmelted layer contains the melt. The melts are arc, plasma or electron beam heated.

### **2.3.5 Tongue and groove crucibles**

They are a modular crucible system consisting of a series of interlocking components that stack together to form a furnace lining or crucible. Tongue and groove crucibles may use a back up of ramming cement behind the crucible, but not within the interlocking grooves. The absence of refractory cement between the ceramic crucible portions improves lining life and melts quality.

### **2.3.6 Wide form crucibles**

They are low, shallow or flat profile vessels with short walls compared to high form crucibles. The crucibles have a very wide opening with an outer diameter that tapers down to a much smaller base diameter. The sidewalls typically have slight outward bow or bulge.

## **2.4 Manufacturing of Graphite Crucible**

Refractories are manufactured from naturally occurring substances in the earth's crust – clay, quartzite, magnesite, chromite, bauxite, graphite etc. All these materials do not occur in their pure form hence needs some treatment before manufacturing. Initial processing may include an extensive survey of the deposit, selective mining, stockpiling by grade, and beneficiation techniques such as weathering, grinding, washing, heavy-media separation, froth flotation etc are employed. Though some can be used without pre-processing, but many must be subjected to heat treatment. Calcination is also been carried out in some of the pre-treatment. Originally, calcinations refer specifically to the

treatment of calcareous minerals to remove CO<sub>2</sub>. The term has come to be used to indicate heat treatment to sinter or burn (dead burn) the refractory grain to stable dense material as well as to decompose minerals. The materials obtained after calcinations are hard burnt materials and they are called grain, clinker or grog. (Chesti 1986).

#### **2.4.1 Beneficiation**

Beneficiation (Chesti, 1986, and Wood,1986) may be carried out physically or chemically. It is used in modifying the characteristics of components, their proportion and distribution in a multi-component system. The desired average particle size of a material can be obtained by reducing the material size through crushing and milling. This process is called comminution and is widely used in ceramic processing. This process is carried out to liberate impurities and reduce size distribution, to disperse agglomerates and aggregates, to reduce the maximum particle size, to increase the content of colloids and to modify the shape of particles.

When the material is large in size, a jaw crusher or cone crushers are used to reduce the average size range down to about 5mm or more. Crushing rolls may be used to reduce less coarse feed to below 1mm, while a hammer mill could be used to reduce size down to about 0.1mm. Ball mills, vibratory mills, fluid energy mills and roller mills are used to reduce the particle size further.

Another method of beneficiation is by froth floatation. In this case the valuable material is been separated from the unwanted ones (gangue). This process entails the use of the difference in affinity of the components to the rising air bubbles within the agitated pulp. Hence the condition of the pulp is varied, the valuable mineral becomes air-arid

(aerophillic) and the gangue becomes water-arid (aerophobic). This then makes the required mineral to be transferred with the air-bubble and this forms a froth float on the surface of the pulp. The froth is then collected and concentrated to the required concentration by adding a deflocculant and allowing the material to settle and then separating it from the excess water. Furthermore, ceramics can be beneficiated using magnetic separation in cases where there are metals in the ore. Also, sorting process can be used for separation i.e. using optical and radioactive properties of the minerals. Other methods include the use of hydraulic current, or electric conductivity processes.

#### **2.4.2 Grog Preparation**

Grog is fired clay; kaolin is first beneficiated through crushing and soaking for 24 hours followed by screening using 200 mesh sieves. The sieved kaolin is dewatered and worked into a plastic body of a stiff consistency. This green body is left in wooden mould and left to dry for seven days. After drying the bricks formed are fired at a temperature of about 1280<sup>0</sup>C.

#### **2.4.3 Sizing and proportioning**

The formed grog is crushed, ground and sieved into different particle sizes. Also the graphite flake that has been beneficiated will be ground and sieved into different particle sizes. To obtain the required density, using the Andreason equation and varying the Andreason parameter, the required proportion of the different sizes can be obtained.

#### **2.4.4 Mixing**

Mixing is carried out in batches. Batch additives may be in the form of a granular material, a powder, a liquid, a chemical solution, an emulsion or slurry. The mixing of this is to combine, distribute, disperse and intermingle the batch material differing in chemical and/or physical form. Mixing must be well controlled to reproducibly mixture i.e. wet the particle, disperse additives, and produce a homogenous batch of the proper consistency.

Mixing is used to improve on the chemical and physical uniformity of the mixture. The mixness of a system refers to the state of that mixture. They can be described after chemical or physical analysis. A mixture is said to be homogenous when the composition do not vary with position when examined. A minimum scale of segregation in a system is determined by the largest particle size in the system. During mixing the minimum scale of segregation and maximum homogeneity are obtained only when agglomerates and viscous additives are well dispersed.

Depending on the forming technique to be used the amount of liquid added are different. For dry pressing 2-6% binding liquid is added. For semi-dry 7-14% binding liquid and for wet pressing 14-24% binding liquid is required. Wet mixing is usually used for hand moulding.



### 2.4.5 Forming processes

Forming (James (1989)) transforms the consolidated system of feed material into a coherent, consolidated body to produce a cohesive body of the desired size and shape. The forming process chosen for a ceramic operation depends on the size, shape, dimensional tolerance of the product, the requisite microstructure characteristics, levels of reproducibility required, capital investment, and productivity considerations. In addition to the surface character after forming, die or mould requirement; energy requirement and safety are put into consideration.

Most refractory shapes are formed by mechanical equipment, but some very large or intricate shapes requires hand moulding in wooden, steel-lined moulds, with loose lines to permit easy removal of plaster of Paris moulds. The forming techniques are dependant on the consistency and rheological response of the material. Coarse granular materials and granulated powders (Reed, 1986) are commonly formed by uniaxial dry-pressing in a hard die or isostatic pressing in a flexible mould. When the degree of saturation of the feed is between 0.01 – 0.5, high-applied stress is needed for the forming i.e. between 20 – 200MPa. But if the degree of saturation is greater than 0.9 with plastic consistency, either extrusion, pressure moulding, injection moulding and jiggering operation is used. In these types of forming a pressure of 1-20Pa are commonly used. A pourable or pumpable slurry ( $DOS \geq 1$ ) is used in conventional casting and the forming pressure is less than 1MPa and this is because the slurry or paste is saturated in a viscous matrix.

Pressing by means of punches in hard metal die commonly called dry pressing, is used for pressing parts thicker than 0.5mm..

#### **2.4.6 Drying and firing process**

For economical reasons, drying should be as fast as possible, however to avoid differential shrinkage that can result in cracking, warping, and shape distortion, rate of drying must be carefully controlled. Generally, larger parts containing more liquid require longer and costlier drying.

Air-drying is the most common means of drying ceramics. Calculated amount of hot air supplies heat to the ware to aid evaporation and compensate for evaporative cooling as it removes vapour from the ware surface. The drying rate is determined by two factors, the rate of liquid evaporation and the rate of liquid migration to the drying front (Harold (1986)). In a saturated body, drying first occurs at a constant rate by the evaporation of the liquid film surrounding individual particles at the ware surface.

Most shrinkage occurs during initial drying stage. Drying shrinkage can be reduced by lowering the concentration of liquid, decreasing the film thickness, or by decreasing the concentration of fines and plastic materials and by adding non-plastics.

Drying of graphite crucible is particularly difficult as the laminar structure restricts movement of water, hence a humid dryer is recommended. A number of changes occur when heating a ceramic prior to sintering these including additional drying, burning out of organic additives, removal of chemically bound water and water of crystallization and decomposition of inorganic precursors or additives. These processes

may be accomplished by a separate heat treatment well below the sintering temperature, or in a controlled series of ramps and isothermal holds in a single heat treatment process. Therefore for a graphite crucible pre-firing to about 700<sup>0</sup>C in open set kilns is advised, so that the surface becomes oxidized. While in muffles, pre-firing should be up to 900<sup>0</sup>C, (the kiln at 1200<sup>0</sup>C), so that the interstices will be filled with coke.

A process described as sintering, in which thermally activated material transport transforms loosely bonded particles and whiskers or fibres into a dense cohesive body, thermally consolidates most ceramic. A ceramic densifies during sintering as the porosity or void space between particles is reduced. Additionally, the cohesiveness of the body increases as inter-particle contact or grain boundary area increases. Both processes depend on temperature and are controlled by rate of material transportation.

The final part of firing a graphite crucible is done in a saggar packed with coke at 1100<sup>0</sup>C. It is done in a saggar to prevent oxidation of the material.

#### **2.4.7 Processing additives**

In processing ceramic materials, several different processing additives must be incorporated in the batch to produce the flow behaviour and desired properties. Most of these additives are added in small quantities and some of them are eliminated on a later stage of the processing. These materials are important materials for a processing, hence their selection and control are very vital and they are the key to a successful processing and/or development of an improved process. Some of the additives are:

#### *2.4.7.1 Binder*

Binders are used to impart strength to a green ceramic body for easy handling and machining. They are used in dry-pressing operations and are also added to plastic extrusion bodies and pastes. But in tape casting, a plasticized binder is needed to give a flexible green tape.

In selecting a binder, there are factors such as ceramic powder, the size of the part, formation mechanism, and the green body density and strength required is all put into consideration. For dry pressing and extrusion, three percent of the binder, based on dry weight of ceramic material is required. In novel or unique forming operations, specialty binders may be used. For instance, pre-ceramic polymer that decomposes to a ceramic on handling and machining are used.

#### *2.3.7.2 Liquids*

Liquids are used in forming of a ceramic green body. They are used as additives in plastic, paste and slurry processing. Water is a cheap and good liquid binder that can be recycled. Organic liquids are used to process water sensitive materials though they are expensive. Other additive includes: plasticizers; lubricants, deflocculants, surfactants, antifoams, etc.

### **2.4.8 Annealing**

This is the final stage involved in the production of ceramic materials. It involves very slow cooling of the fired crucibles in the kiln. In continuous kilns, cooling takes place as the fired crucibles move towards the discharged point since it is moving from the

firing point, while in batch kilns the fire is put off and the damper closed, and heat loss is mostly by radiation, which is gradual. This cooling takes about the same time as the heating of the goods to the finished or maturing temperature.

Successful cooling of matured crucible requires a careful consideration of the physical, chemical changes, which may occur. Rapid cooling can cause cracking either immediately or after sometime. Hence slow cooling is needed.

## **2.5 Recent Works**

In the Chemical Engineering Department, Ahmadu Bello University, Zaria, the recent work done on the production of graphite crucible was at the undergraduate level. Some beneficiation of Gayama and Bauchi graphite (Awareng, 1997 and Sekula 2002) was carried out. Also production of graphite crucible using tar and clay as binding materials (Kwada,(1998), Alao (1999), Adefila, (2000) and Olaniyan (2001)) has been carried out and the forming techniques used is the pressing method. In those works, it started with a laboratory scale crucible and the largest size obtained was the production of a 15kg crucible (Adefila 2000). There were notable short comings in the works such as non determination of the optimum condition for the beneficiation of the graphite, and the size produced are not large enough to be tested in the steel industry.

## CHAPTER THREE

### 3.0 EQUIPMENT, MATERIALS AND METHODOLOGY.

#### 3.1 EQUIPMENT

The various equipments used for this work includes.

- (i) Geological Hammer
- (ii) JawCrusher – Mc No. 17769
- (iii) Grinding machine – Mc. No. 17834
- (iv) Tamson mechanical shaker – Type R4.
- (v) Tyler sieves with different mesh sizes between 100 $\mu$ m -2100 $\mu$ m
- (vi) Denver floatation machine – Type D12.
- (vii) Beakers
- (viii) Digital weighing balance
- (ix) Clay pot (in place of a saggar).
- (x) Density bottle
- (xi) Buckets (sizes between 200mls -20liters).
- (xii) Stirrer (wooden 50cm)
- (xiii) Pressing mould (female – POP mould and male – metal mould)
- (xiv) Gallen Kamp electric Oven model OV – 420 (40<sup>0</sup>c – 260<sup>0</sup>c)
- (xv) Furnace – type 420 (100<sup>0</sup>c – 1350<sup>0</sup>c)
- (xvi) Heavy – duty drilling machine

- (xvii) Wooden pattern
- (xviii) Kerosene stove
- (xix) Sintered Crucible
- (xx) Locally made kiln
- (xxi) Harmer mill
- (xxii) Silicon paper
- (xxiii) Hack saw
- (xxiv) Polishing machine
- (xxv) Strip grinder
- (xxvi) Cotton wool
- (xxvii) Leitz ORIHOLUX II POL-BK Polarising and Reflected light Research microscope.
- (xxviii) Camera
- (xxix) Kodak film
- (xxx) Thermolyne Temcometer Controller Model OPL-29103

### **3.2 Material**

- (i) Turpentine
- (ii) Kerosene
- (iii) Sodium Carbonate (25% solution)
- (iv) Water
- (v) Xylene
- (vi) Kaolin (Kankara clay)

(vii) Silicon powder (BDH)

(viii) Charcoal

### **3.2.1. Procurement of graphite.**

The graphite used for this work was procured from Duchin Hai in Bauchi State. We went with a geologist. We were able to obtain the graphite from an old pit which is filled with debris. The method of sampling used is selective mining. The graphite was used by the local people to decorate their houses. The problem encountered was the unmotorable road in the area. The road is plied only on their market day and at some point the passenger gets down and walks some distance and sometimes the passengers would have to push the vehicle. The road to the village is flooded and erosion is eating it up.

### **3.2.2 Procurement of coal tar.**

In Sabon –Gari market there are two types of coal tar available. At room temperature one type is soft and the second type is hard.

## **3.3 Experimental Procedure**

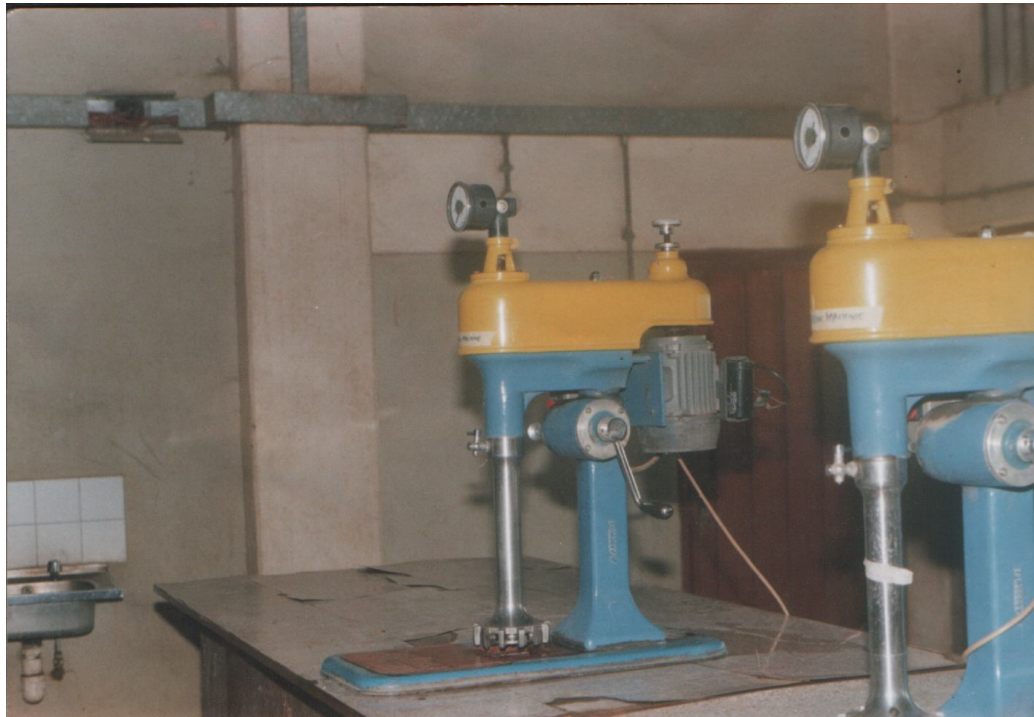
This section gives a detailed systematic procedure for the production of the graphite crucible.

### **3.3.1 Beneficiation of graphite ore**

The graphite ore sample that was obtained from Duchin Hai (in Bauchi State) was beneficiated using a laboratory Denver froth floatation machine (model: D12). In the course of beneficiation, different chemical and operating conditions



used were monitored. This was carried out by varying the quantity of collector (kerosene) first, while other conditions were kept constant. In separate runs, following the simple unifactorial principle, optimum quantities of frothier (turpentine) and modifier ( $\text{Na}_2\text{CO}_3$ ) were determined. Also the optimum agitation time before and after addition of the reagent was obtained. All the experiments were carried out at a froth floatation machine speed of 50 rpm. The Denver Froth Flotation equipment is shown pictorially in Plate 3.1



**Plate 3.1: The Denver Froth Flotation Equipment.**

### **3.3.2 Preparation of clay grog**

The clay that was obtained from Kankara (Kankara village, Katsina state) was soaked in a large bucket for two days. It was then thoroughly stirred and allowed to soak for one more day after which it was washed by sieving using a

mesh sieve size of 73  $\mu\text{m}$ . While washing, it was the upper suspension layer that was taken to prevent carrying over the silica. The washed clay was allowed to settle so that the clay could sediment to the bottom and the supernatant water layer on top was decanted. The clay was moulded into bricks, dried under the shade for seven days and then fired at a temperature of about  $1300^{\circ}\text{C}$  for six hours. It was then allowed to cool. Then it was crushed and sieved into various fractions as shown in Table3.1

### **3.3.3 Flake size analysis**

Different sieve sizes up to  $1000\mu\text{m}$  were fixed into each other and a 100g of raw Duchin Hai graphite was measured and poured into the  $1000\mu\text{m}$  sieve. It was then fixed on the sieve shaker and put on for 15 minutes. Then the different fraction found in each sieve was weighed.

### **3.3.4 Density of graphite**

The density of the raw graphite and the beneficiated samples was determined using the xylene density method (Emma 2000).

### **3.3.5 Determination of carbon content**

4g each of the raw and beneficiated sample was weighed into different sintered glass crucible and put in a furnace at a temperature of  $1200^{\circ}\text{C}$  for about 48 hours (a cumulative addition of time when electricity was available was used to

get the 48 hours. This is due to light failure from time to time). At the end of the 48 hours, the crucible was transferred into desiccators. The sample was then weighted after cooling. Then put back in the furnace again for one hour and back to the desiccators, then weighed. This latter procedure was repeated until a constant weight was obtained. (ASTM (1977)).

### 3.3.6 Determination of the clay grog particle size distribution

Using the Andreason equation (Chesti 1986),

$$P = 100 \left[ \frac{d}{D} \right]^n \quad \text{where } n = 0.7 \text{ (Ahmed.)}$$

**Table 3.1: Particle Sizes Distribution of Crushed Clay Grog**

Grain Size (mm)	Particle size distribution.	Percentage (%)
2.1 – 1.0	80.85	0.26
1.0 - 0.5	81.76	0.26
0.5 - 0.375	91.08	0.29
0.375 -	61.16	0.19

### 3.3.7 Preparation of the female mould (die)

The wooden pattern used to produce the female mould was obtained by turning a cylindrical wood of 370mm diameter by 500mm length. A template with the shape of the outer diameter was made using a metal sheet. As the wood was

turned and machined, the template was used to mark the wood until the required shape was obtained. The top diameter of the wood mould is 218mm, the bottom diameter is 162mm and the height is 265mm

From findings (Olanipekun (1998)) a ratio of 6:4 of plaster of Paris to water by volume was used in the production. Slip casting method was used.

Six bowls of Plaster of Paris powder were sieved through a 500 µm sieve size into a bucket containing four bowls of water. The powder was left in the water for about 5 minutes to soak. After soaking, it was stirred continuously until no lump was found in the mixture and air bulbs were no longer seen in it. After that the mixture was left for 30 minutes to thicken.

While that was going on, Vaseline was rubbed over the wooden pattern that was used for the casting. It then was put in a bucket where the Plaster of Paris mixture was to be poured. Therefore, it was put in the bucket and was well centered, then the thick mixture was poured into the bucket after 30 minutes. The wood gave the cylindrical bucket a hollow cavity which forms the external shape of the crucible (Plate 3.2).



**Plate 3.2: The Wooden Pattern Used for Producing the Female Mould.**

Scale 1:2.44



**Plate 3.3: The Female Mould**

Scale 1:2.75

### **3.3.8 Preparation of the male mould**

A cast iron cylindrical rod of size 300mm diameter by 450mm length was shaped by a lathe machine to give the shape of the inner cavity of the crucible.

The machined rod is shown in Plate 3.4. The male mould was also formed using a template that has the shape of the inner part of the crucible.



**Plate 3.4: The Male Mould**

Scale 1:2.5

The male mould has a top diameter ( inner diameter of the crucible) of 176mm, bottom diameter 118mm and height of 235mm. The upper part to the top diameter of 216mm and the last part has a diameter of 250mm

### **3.3.9 Selection of batch composition.**

In choosing the composition of the crucible, the following factors were considered. The graphite to clay grog ratio, the size fraction of the grog, the proportion of the different fraction and the quantities of coal tar and silicon powder were considered.

Harold (1986) reported that, the graphite required for crucible production is 30-50%. Based on this and the calculation carried out in Appendix A, Olanipekun carried out experiment and found 30wt% graphite and 70wt % kaolin grog was the best .According to Chesti (1986) the best largest grain size for refractories is 10% of its thickness. Based on this, since the thickness of the crucible formed is 21mm, the largest grain size required for this work was 2.1mm. Hence the largest grain size of the clay grog was taken to be 2.1. Three other fractions were taken (1.0, 0.5, 0.375). These other fractions were taken to give good packing.

The ground grog was sieved using a Tamson mechanical shaker, Type R4 and the appropriate Tyler sieves were used to obtain the required fractions of the grog. The sieving operation took about one hour for each batch at a 100% vibration



The quantity of coal tar required was found to be 35wt% of the sum weight of graphite and clay grog while Harold reported 2wt% silicon powder of the sum weight of graphite and clay grog was required.

### **3.3.10 Forming of the crucible**

Two different types of coal tar were used for this experiment.

In each case, the 35wt% of coal tar was heated until it was fully melted and then 2 wt % of silicon powder was added and stirred until it was completely mixed (the 2weight % was of the sum weight of graphite and clay grog). Then 30wt% graphite powder was added and stirred until the mixture is completely mixed. While it was on fire, the different fractions of the 70wt% clay grog were mixed together in a container and were added to the mixture on the fire gradually. The mixture was mixed thoroughly until a homogenous mixture was obtained. The mixture was left covered and after every 5 minutes, it was opened and stirred. This continued until the temperature reached about 250°C.

While the graphite-clay, mixture was on fire, the male mould was fixed to the hydraulic press. The male and the female mould were pre-heated.

When they were heated, the mixture was poured into the female mould and the male mould was inserted to press the mixture into a crucible. The forming process was such that as the male mould was introduced into the female mould, it was continuously rotated and removed gradually while still rotating. The crucible was left for three day in the female mould to set and shrink so that it could be removed easily. The removed crucible was left to dry under shade for seven days. Two

crucibles measuring top diameter of 216mm, bottom diameter 176mm and height of 260mm were successfully formed in this manner.

The pictures of the forming procedure are shown on Plates 3.5 – 3.9



**Plate 3.5: Mixing of the Materials on the Heating Stove.**



**Plate 3.6: Heating of the Male Mould.**



**Plate 3.7: Setting of the Female and Male Moulds Prior to Pressing.**



**Plate 3.8: Forming of the Crucible:**





**Plate 3.9: The Green Crucible Produced**

Scale 1:3.2

### **3.3.11 Firing of the crucible.**

The crucible formed was packed in a clay pot using fine charcoal powder to fill both the inside of the crucible and the space between the pot and crucible. The clay pot was covered with another pot and sealed using kaolin paste. The pot was placed in a local kiln and fired to a temperature of  $900^{\circ}\text{C}$  for 3 hours.

To monitor the temperature of the Kiln, a thermocouple (Thermolyne Temcometer Controller Model OPL-29103) was fixed to the local Kiln. The firing schedule for crucible (B) is shown in Table 3.2.

**Table 3.2 Firing Schedule for the Crucible (B)**

Time (Hour)	Temperature ( $^{\circ}\text{C}$ )
0.5	150
0.5	200
0.5	250
0.5	300
0.5	350
0.5	450
0.5	550
0.5	650
0.5	750
1.0	800
1.0	900

To get to the temperature of  $900^{\circ}\text{C}$  two different methods were used. For the first crucible (A) the kiln was fired from the onset using its two burners while for the second crucible (B), gradual heating was carried out using first, a single burner, then the second burner was introduced later to increase it to the required temperature. After firing, the burners were removed and the kiln was closed and allowed to cool via radiation till the following day.

The picture of the packing procedure is shown on Plates 3.10



**Plate 3.10: Preparation of the Crucible for Firing**

Scale 1:4

### **3.4 Microstructure Examination**

Microstructural examination of opaque specimens like the graphite crucibles require that specimen surface is highly polished. The step for obtaining this are



sectioning, mounting (escapulation), grinding and polishing, and finally, microscopic examination.

#### **3.4.1. Sectioning**

- i. Cubes of approximately 10mm x 10mm x 10mm dimension were cut from the crucible.
- ii. The surfaces of the cut specimen were cleaned with dampened cotton wool to remove the debris.

#### **3.4.2 Mounting**

- i. Each of the specimen was placed in the steel mould with the face to be polished (perpendicular to the original pressing direction) downward.
- ii. About 10cm<sup>3</sup> of polyester to 3 drops of MEK peroxide catalyst were added and thoroughly mixed.
- iii. About 2 minutes later, a drop of accelerator was added and mixed.
- iv. The resulting mixture was immediately poured into the steel mould to the level that just covered the specimen.
- v. It was left over night to set.

#### **3.4.3 Grinding and Polishing**

The system of grinding and polishing adopted in this investigation comprises successive silicon carbide papers attached to stripped grinder for initial grinding, and 1 micron alumina impregnate polishing wheel for final polishing. The corresponding steps are outlined as follows for each of the samples.

- i. The sample was grinded in one direction using a stripped grinder of 240 grit size silicon carbide paper. Periodically, the surface was observed for homogeneity in the surface grinding. At the end the specimen was washed.
- ii. The same procedure was repeated for 320, 400 and 600 grit sizes. At the end of which a finely ground surface was obtained.
- iii. The polishing cloth on the polishing wheel was impregnated with 1-micron alumina powder made into paste by addition of water.
- iv. The polishing machine was put into operation, and the cloth-covered polishing wheel rotated in anticlockwise direction.
- v. The finely ground surface was brought in contact with the polishing cloth and moved in the opposite (clockwise) direction to increase the relative velocity of contact.
- vi. Periodically, the polishing surfaces were washed and were observed for clear microstructure in the microscope.
- vii. The process continued until the microstructure was found satisfactorily clear.

#### **3.4.4 Microscopic examination**

Examination of the polished surfaces was carried out using Leitz ORIHOLUX II POL-BK Polarising and Reflected light Research microscope at a magnifications of 100. Photographic records of the microstructure were made using the incorporated camera.

## CHAPTER FOUR

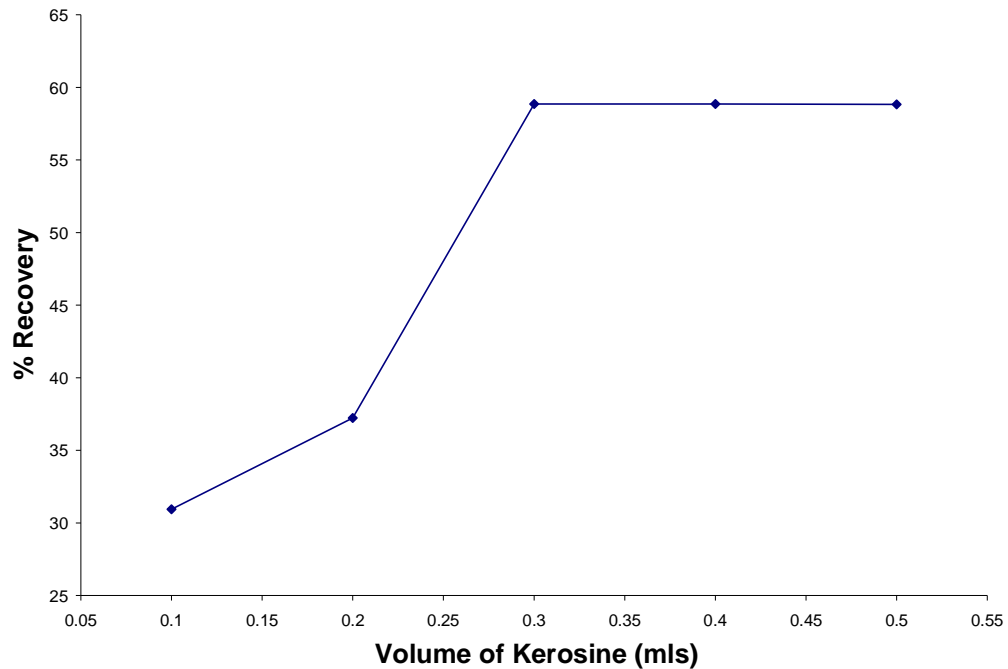
### 4.0 RESULTS AND DISCUSSION

#### 4.1 Results

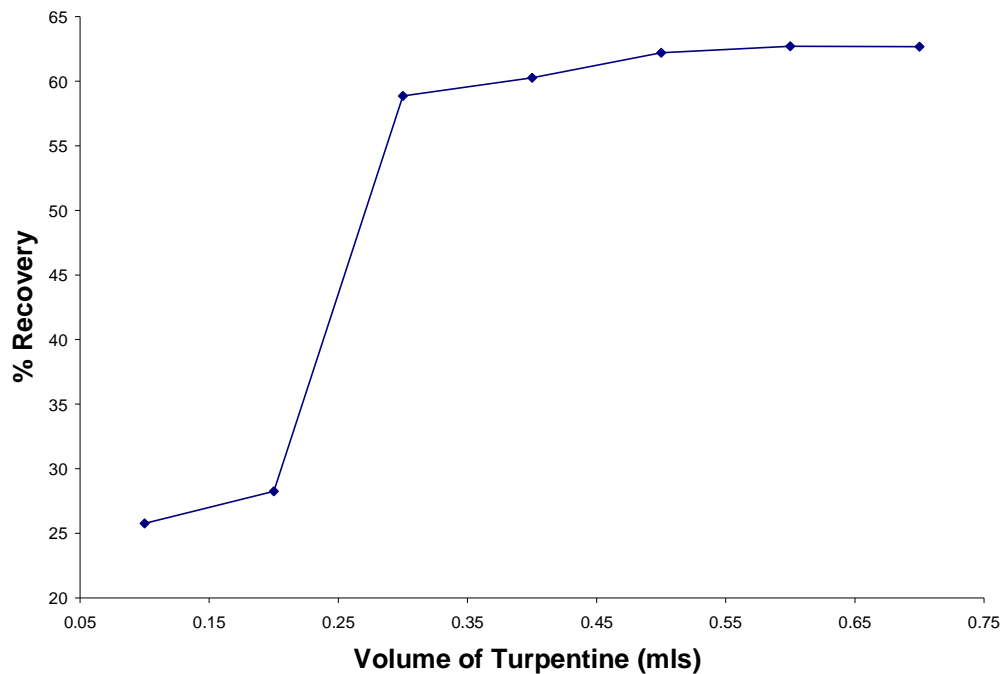
The results of the experimental investigations are reported here and discussed later in section 4.2

##### 4.1.1 Chemical and operating conditions of the frothed graphite pulp.

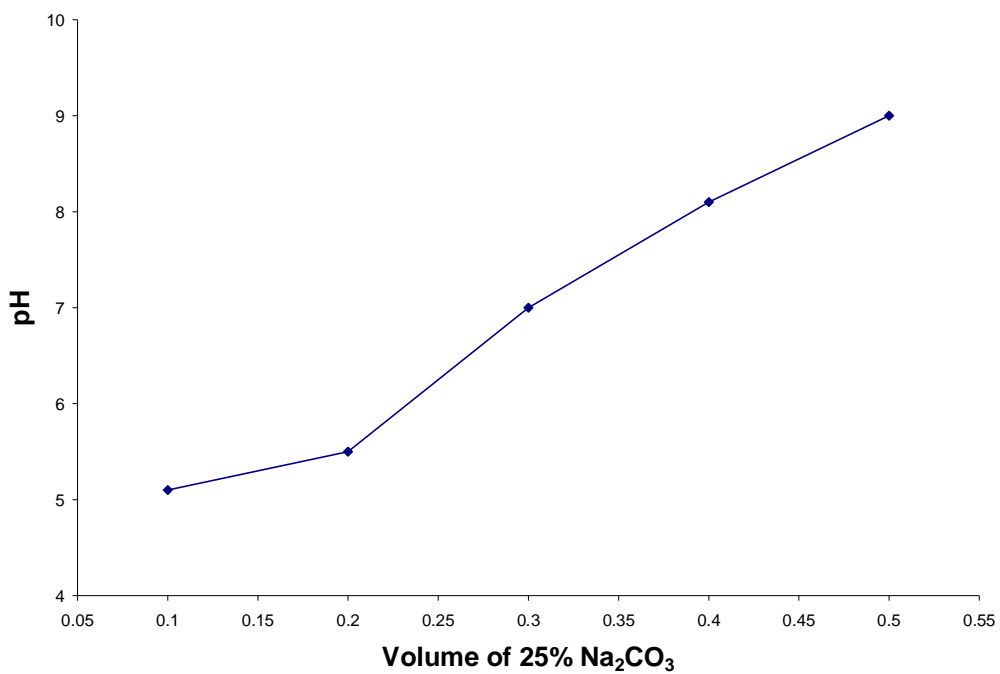
Figure 4.1 -4.5 presents the results obtained from the optimum beneficiation of the graphite.



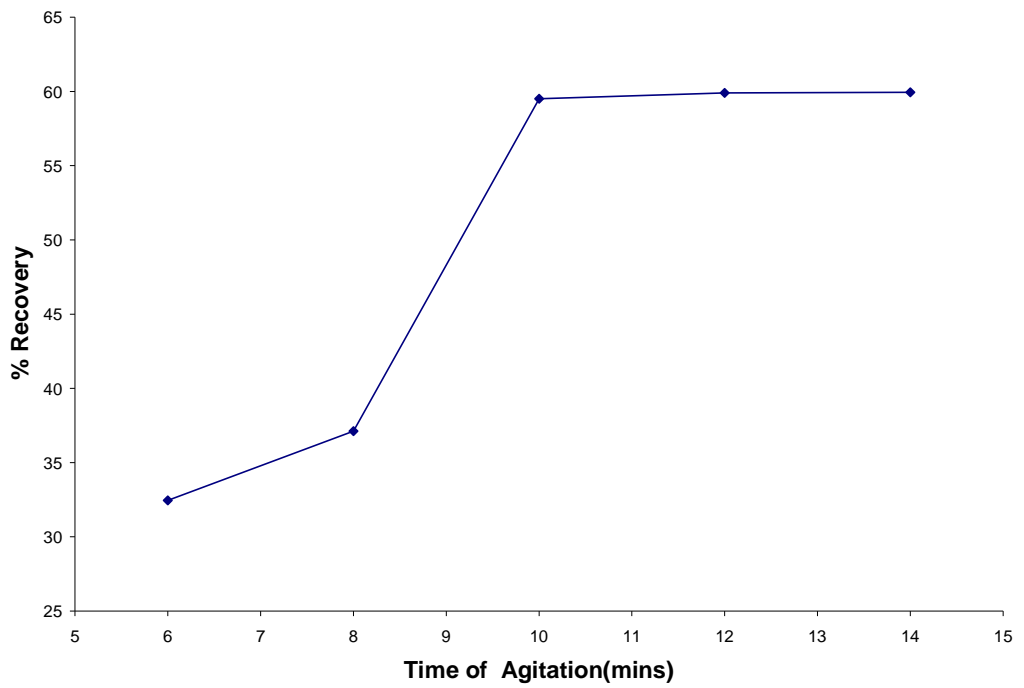
**Figure 4.1: Effect of Kerosine on % Recovery**



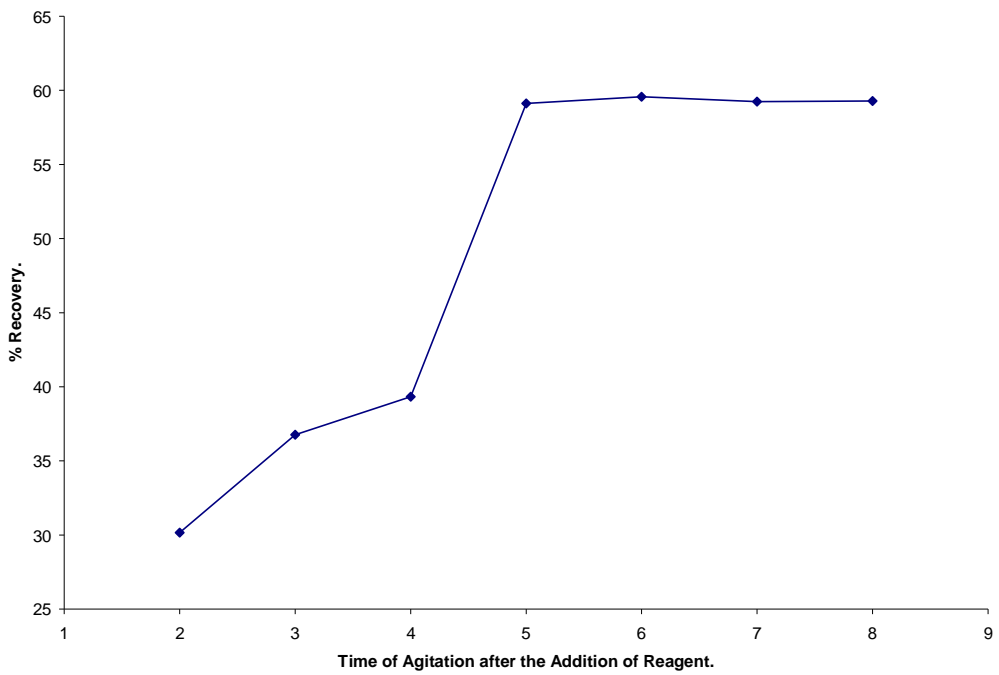
**Figure 4.2 Effect of Turpentine on % Recovery**



**Figure 4.3: Effect of 25% Na<sub>2</sub>CO<sub>3</sub> on % Recovery**



**Figure 4.4: Effect of Time of Agitation before the addition of Reagent on % Recovery.**



**Figure 4.5: Effect of Time of Agitation After the Addition of Reagent on % Recovery.**

#### 4.1.2 Characterisation of the raw ore and beneficiated graphite

Table 4.1 shows the sieve size analysis of the raw sample while Table 4.2 shows the value of the carbon content and density of the different sizes of the beneficiated graphite. Table 4.3 also shows the carbon content and density of the raw and beneficiated graphite.

**Table 4.1: Flake Size Analysis of the Raw Bauchi Graphite Ore**

Sieve Size of Fraction ( $\mu\text{m}$ )	+1000	-1000+500	-500+355	-355+100	-100
Amount retained (%)	6.40	17.20	25.80	30.40	20.20

**Table 4.2: Density, Ash and Carbon Content of Bauchi Graphite by Size Fraction**

S/N	Sample	Flake Size Fraction ( $\mu\text{m}$ )	Average graphite Recovery (wt %)	Ash Content (wt %)	Carbon Content (wt %)	Density $\text{kg/m}^3$
1	A	-1000+500	56.00	12	88	2,260
2	B	-500+355	59.30	18	82	2,240
3	C	355+266	68.00	22	78	2,230
4	D	-255+100	63.33	22	78	2,260
5	E	-100	68.45	14	86	2,240
6	F	Raw Sample		58	42	2,480

**Table 4.3: Density, Carbon and Ash Content of Bauchi Raw and Beneficiated graphite**

<b>S/N</b>	<b>Sample</b>	<b>Ash Content (w%)</b>	<b>Carbon Content (wt %)</b>	<b>Density (kg/m<sup>3</sup>)</b>
A	Raw	58	42	2,480
B	Beneficiated	18	82	2,250
C	Pure graphite (literature value)			2,260

#### **4.1.3 Moulds used for the formation of the crucible**

Plate 3.2 shows the picture of the wooden pattern use for the production of the female mould. Plate 3.3 shows the picture of the female mould. Plate 3.4 shows the picture of the male mould.

#### **4.1.4 Graphite crucible formed**

Plate 4.1 shows the picture of one of the crucible formed.



**Plate 4.1: The Graphite Crucible Produced**

Scale 1:1.78



#### **4.1.6. Microstructural result.**

Plate 4.2 shows the microstructure of the fired crucible



**Plate 4.2: Microstructure of the Crucible Produced**

## **4.2 Discussion of Results.**

### **4.2.1 Chemical and operating conditions of the frothed graphite pulp.**

It can be observed from Figure 4.1 that for 50g of raw graphite ore in 300mls of water 0.3ml of kerosene (which acted as the collector) gave the maximum recovery of the graphite at 60%. The kerosene collected the pure graphite from the froth and left the unwanted gangues in the tailings. From Figure 4.2 the amount of turpentine, which acted as the frothier (stabilizer), required for optimum recovery was 0.5ml. Figure 4.3 showed that the pulp solution could be regulated to pH of about 7 with 0.3ml of  $\text{Na}_2\text{CO}_3$  per 50g of graphite ore in 300mls of water. This satisfied the requirement that the pH of the pulp should be between 6.5 to 8.0 (Cirkel (1966)). On agitation time it can be observed from Figure 4.4, that the best agitation time before the addition of reagent was 10 minutes while from Figure 4.5, 5 minutes agitation time was best after the addition of reagents. The agitation was carried out at a speed of 50 rpm. This agitation was necessary so as to have a homogeneous mixture.

### **4.2.2 Characterisation of the raw ore and beneficiated graphite**

From Table 4.1, it can be observed that the ore flake size distribution in which 93.5 wt% of the material was below particle size of 1mm. This showed that the graphite had large flake size which was good for the production of refractory items such as crucible. The larger the flakes size the better the thermal shock resistance.

From Table 4.2, it was observed that the coarsest fraction (sample A - - 1000 + 500  $\mu\text{m}$ ) had a density of 2,260  $\text{kg}/\text{m}^3$  which was the same with the literature value (Cirkel (1966)) for pure graphite. This could be attributed to the presence of less impurity, but the finer samples had lower density which could be attributed to the presence of more impurities. This conforms with the result obtained for the ash content except in the case of the finest sample (-100  $\mu\text{m}$ ) which had a lesser ash contents. From the table it was found also that, the average percentage recovery increases with the decrease in flake size. This could be as a result of easier floating of the flake as it size decreased, hence more could float even though with more impurities.

From Table 4.3, it can be observed that the average density of the beneficiated sample (2,250  $\text{kg}/\text{m}^3$ ) which closely agrees with the literature value of 2,260  $\text{kg}/\text{m}^3$  while that of the raw material was found to be 2,480  $\text{kg}/\text{m}^3$ . This high value for the raw material could be as a result of impurities present in the sample with higher densities. For graphite ore occurs with impurities such as sand,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and oxides of metal which have higher density than graphite.

#### **4.2.3 Moulds used for the formation of the crucible**

Plate 3.2 shows the picture of the pattern used to produce the female mould while Plate 3.3 and 3.4 show the picture of the female mould and the male mould used for the formation of the crucible. The moulds were produced locally using the available machine. They are symmetrical. This could be reproduced.

#### **4.2.4 Graphite crucible formed**

From the result obtained from preliminary study carried out earlier, two crucibles pressed using two different types of coal tar were formed successfully.

#### **4.2.5 Firing of the crucible.**

During the firing process the first crucible (A) came out well except for the part that, the pot used as saggar got broken. That part of the crucible got oxidized. For the second crucible (B), as the firing progresses, at a temperature of about 700°C, the clay pot used as saggar blew open. This may have been as a result of the pressure build up inside the pot since the pot was impermeable to gas penetration.

In earlier experiment carried out (Olaniyan 1998) the charcoal was densely packed and fired, but there was no problem of explosion of the sample. The explosion experienced in the case of this study could be as a result of the clay pot – used instead of the conventional saggar. The saggar normally used are made in such a way that, it has pore spaces, so that, when any gas is formed, it can find a way to escape. But the clay pot used had less gas permeability and it did not allow gases to pass through easily. And since the charcoal used in sample B was densely packed, the gas from the crucible could not find escape route, which made the gas to build up much pressure and consequently blew open the cover at temperature of 700°C and then gave way to air to come in contact with the crucible. Since

graphite burns in presence of air at temperature of 630<sup>0</sup>C (Cirkel (1966)), the crucible then oxidized.

#### **4.2.6 Microstructural result**

From Plate 4.2, it was observed that all the materials (graphite, kaolin, coal tar , silicon powder) used for the formation of the crucible were found present in the picture which shows that the mixing procedure used was appropriate. It is seen that the coal tar filled the part that were porous.

## CHAPER FIVE

### 5.0 CONCLUSIONS

Based on the study carried out, it can be concluded that

- 1) The optimum quantity of Kerosene, Turpentine and 25%  $\text{Na}_2\text{CO}_3$  needed to float 50g graphite in 300 mls of water during its beneficiation by froth flotation method was 0.3, 0.5 and 0.3mls respectively
- 2) To get the best yield, the time required to agitate 50g graphite in 300 mls of water during it's beneficiation by froth flotation method was found to be 10 minutes before additions of reagent and 5 minutes after addition of the reagents.
- 3) The beneficiated graphite is of high quality, which makes it good for production of crucible.
- 4) The mould required for life size can be produced locally.
- 5) Two life size graphite crucible were successfully formed by pressing method using tar as binder
- 6) The formed crucibles could not be fired successfully due to lack of suitable firing saggars.

## **CHAPTER SIX**

### **6.0 RECOMMENDATIONS**

The following recommendations are made from the course of this study.

- (i) A saggar suitable for firing 30kg size crucible should be procured and used during the next study.
- (ii) Facilities should be provided to carry out test on some of the properties of the crucible, such as permeability, thermal shock resistance and resistance to slag.
- (iii) A hot mixer for mixing the materials should be provided
- (iv) Further study on the composition of the Bauchi graphite should be carried out.

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## APPENDIX A

### Calculation of the ratio of graphite to kaolin to be mixed

The quantity of kaolin and graphite to be mixed are calculated.

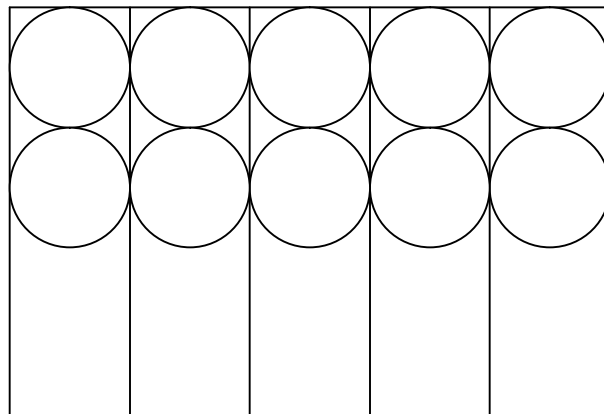
Consider the graphite sample to be as shown in fig. A.1



**Figure A.1: Grain shape of kaolin or graphite**

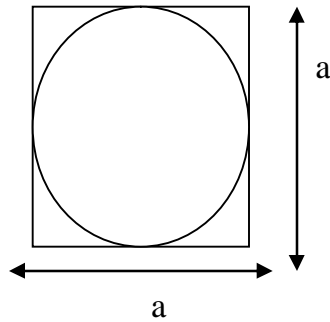
For this calculation, it is assumed that:

- 1) The graphite grain touches another graphite grain and that of kaolin touches another kaolin grain
- 2) The sample are spherical with a diameter “a”.
- 3) The grains are arranged as shown in fig A.2



**Figure A.2: Arrangement of the Grains.**

Considering a unit of volume (fig. A.3).



**Figure A.3: Unit Volume of the mixture graphite and kaolin grain.**

Taking Graphite to be the spherical one and kaolin the square part.

The volumetric ratio of the graphite to the kaolin is

$$\frac{\pi a^3}{6} : a^3$$

$$53.2\% : 46.8\% \quad - \quad \text{volume basis}$$

$$\text{But volume} = \frac{\text{weight}}{\text{Density}}$$

$$\frac{\text{Wt graphite}}{\rho \text{ graphite}} = \frac{\text{Wt kaolin}}{\rho \text{ kaolin}}$$

$$\text{Wt kaolin} = \frac{53.2 \times 2.67}{2.26}$$

$$= 62.85 \text{ wt \%}$$

$$\text{Wt graphite} = 37.15 \text{ wt \%}$$

From this theoretical value, experiment was carried out (Olaniyan 2001.) and it was found that the best weight fraction needed to be mixed is 30wt% graphite to 70 wt% kaolin.

**Clay Ratio**

$$\begin{aligned} \text{Thickness of the crucible} &= (218 - 176)/2 \\ &= 42/2 \\ &= 2.1 \end{aligned}$$

Using the Anderson equation

$$P = 100 [d/D]^n$$

Where n=0.7 (Ahmed)

<b>Grain Size (mm)</b>	<b>P article size distribution.</b>	<b>Percentage</b>
2.1 – 1.0	80.85	0.26
1.0 - 0.5	81.76	0.26
0.5 - 0.375	91.08	0.29
0.375 -	61.16	0.19

## APPENDIX B

### Results obtained from the beneficiation of graphite

#### Beneficiation

**Table B.1 Percentage Recovery with Varying Volume of Kerosene Used.**

Vol of kerosene (ml)	1 <sup>st</sup> Batch	2 <sup>nd</sup> Batch	3 <sup>rd</sup> Batch	Average	% Recovery
0.1	15.02	15.70	15.70	15.47	30.94
0.2	18.35	19.00	18.50	18.62	37.23
0.3	29.38	29.50	29.40	29.43	58.85
0.4	29.40	29.40	29.50	29.43	58.85
0.5	29.35	29.40	29.50	29.42	58.83

**Table B.2 Percentage Recovery with Varying Volume of Turpentine.**

Vol of turpentine (ml)	1 <sup>st</sup> Batch	2 <sup>nd</sup> Batch	3 <sup>rd</sup> Batch	Average	% Recovery
0.1	12.54	13.50	12.60	12.88	25.76
0.2	14.38	14.20	13.78	14.12	28.25
0.3	29.38	29.50	29.40	29.43	58.85
0.4	30.01	30.50	29.90	30.14	60.27
0.5	31.00	31.80	30.50	31.10	62.20
0.6	31.05	32.00	31.00	31.35	62.70
0.7	31.01	31.00	32.00	31.34	62.67

**Table B.3 pH Value for Different Volume of 25% Na<sub>2</sub>CO<sub>3</sub> Solution Added**

Vol of Na <sub>2</sub> CO <sub>3</sub> (ml)	1 <sup>st</sup> Batch	2 <sup>nd</sup> Batch	3 <sup>rd</sup> Batch	Average
0.1	5.0	5.2	5.0	5.1
0.2	5.5	5.4	5.6	5.5
0.3	7.0	7.1	7.0	7.0
0.4	8.0	8.0	8.2	8.1
0.5	9.0	9.1	9.8	9.0

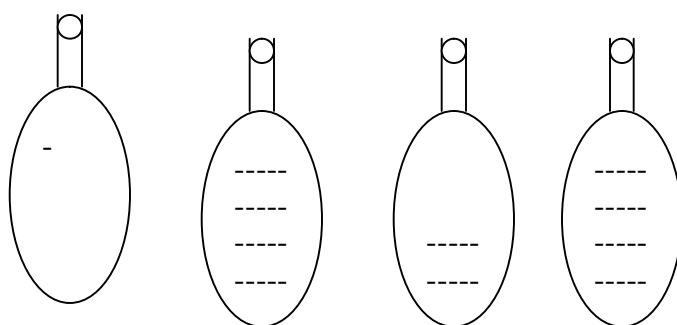
**Table B.4 Percentage Recovery with Varying Time of Agitation before the Addition of Reagents**

Time (Min)	1 <sup>st</sup> Batch	2 <sup>nd</sup> Batch	3 <sup>rd</sup> Batch	Average	% Recovery
4	10.92	11.02	10.83	10.92	21.84
6	16.34	16.01	16.34	16.23	32.46
8	18.34	18.34	19.01	18.56	37.12
10	29.38	29.38	30.50	29.75	59.50
12	29.38	30.01	30.45	29.95	59.90
14	29.39	30.05	30.50	29.97	59.94

**Table B.5 Percentage Recovery with Varying Time of Agitation after the Addition of Reagents**

Time (Min)	1 <sup>st</sup> Batch	2 <sup>nd</sup> Batch	3 <sup>rd</sup> Batch	Average	% Recovery
2	15.23	14.00	16.01	15.08	30.16
3	18.23	18.50	18.41	18.38	36.76
4	19.65	19.75	19.60	19.67	39.33
5	29.38	29.50	29.80	29.56	59.12
6	29.40	29.46	30.50	29.79	59.57
7	29.42	29.95	29.50	29.62	59.24
8	29.92	29.50	29.50	29.64	59.28

Xylene Density of the Beneficiated Sample



Weight of Empty bottle = 27.05g

Weight of bottle + Xylene = 69.44g

∴ Weight Xylene = 42.39g

Volume of Xylene = 50mls

Density of Xylene = 0.8479

**Table B.6 Density of Beneficiated and Raw Samples**

<b>Sample</b>	<b>Mass of Sample (g)</b>	<b>Mass of Xylene (g)</b>	<b>Vol. of Xylene (mls)</b>	<b>Vol. of Sample = 50 – Vol. of Xylene (mls)</b>	<b>Density of Sample = (g/mls)</b>
A	7.82	39.46	46.54	3.31	2.26
B	7.34	39.62	46.72	2.82	2.24
C	7.35	39.71	46.84	3.16	2.23
D	8.5	39.12	46.14	3.86	2.26
E	10.08	38.74	45.70	4.30	2.24
Raw sample	7.82	39.72	46.85	3.15	2.48

**Table B.7 Carbon Content of the Beneficiated and Raw Sample**

<b>S/N</b>	<b>Sample</b>	<b>Sieve size (lm)</b>	<b>Average recovery (%)</b>	<b>% weight ash</b>	<b>% Weight of carbon</b>
0.1	A	+ 500 - 1000	56.00	12	88
0.2	B	+ 350 - 500	59.30	18	82
0.3	C	+ 255 - 350	68.00	22	78
0.4	D	+ 100 - 255	63.33	22	78
0.5	E	- 100	68.45	14	86
06	Raw			58	42

