THE PRODUCTION OF β - SIALON BY CARBOTHERMAL REDUCTION AND NITRIDATION OF KANKARA CLAY

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Declaration

I, Muhammad Bello Janbako, declare that this thesis is solely the result of my work and has never been submitted anywhere for any degree. All literature cited have been duly acknowledged in the reference.



Muhammad, B. J.

CERTIFICATION

This Project thesis entitled THE PRODUCTION OF β-SIALON BY CARBOTHERMAL REDUCTION AND NITRIDATION OF KANKARA CLAY by MUHAMMAD BELLO JANBAKO meets the regulations governing the award of the degree of Master of Science (Chemical Engineering) of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to my family.

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ABSTRACT

The production of (β-sialon - a ceramic material that can be used in the production of refractory articles for use in the iron and steel industries, chemical and process industries, non ferrous metallurgical industries etc, from local1y avai1able rawmaterials using locally assembled production facility has been attempted, p-Sialon can be prepared from natural aluminosi1icate raw materials by carbothermal reduction and nitridation at high temperatures (> 1100°C). To produce β-sialon from locally available aluminosi1icate raw materials, Kankara clay which is a good local kaolinitic clay was chosen.

Carbothermal reduction of Kankara kaolinitic clay was therefore carried out in this study, with Onyeama Coal serving as the carbon source for the reduction reaction in nitrogen gas atmosphere. Proximate analysis on the Onyeama Coal has shown that, the coal is rich in the amount of fixed carbon (85.9 wt.%), less ash content (5.1 wt.%) and moderate volatile matter (8.91 wt.%).

A local production facility to carry out the carbothermal reaction has been set up. A reaction chamber from locally available raw materials was designed and fabricated using investment casting technique. An existing gas-fired furnace design partially constructed, was completed, assembled and tested. From the experimental results, the furnace can be operated up to 1060°C without incorporating a blower for about seven hours.

The bulk nitrogen analysis of the sialon product formed has shown that very small concentrations of β-sialon were obtained using the production facility under the operating conditions achieved. At nitrogen flowrate of 72.4 ml/s, a peak temperature of 1360°C was achieved during the first production run which lasted for about 13 hours resulting in about 2.97 wt% (β-sialon.

Similarly for the second production run which lasted for about five hours at nitrogen flowrate of 143.68 ml/s, a peak temperature of 1260°C was achieved resulting in about 3.32 wt.% β-sialon. During the third production run which lasted for about four hours at nitrogen flowrate of 102.23 ml/s. a peak temperature of 1315°C was achieved resulting in about 3.23 wt.% β-sialon.

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LIST OF ABBREVIATIONS

Adm.	:	Administration
ASTM	:	American Society for Testing and Materials
atm.	:	Atmosphere
Co.	:	Company
deg.	:	degree
e.m.f.	:	electromotive force
Eng.	:	Engineering
Engr.	:	Engineer
LOI	:	Loss on Ignition
LPG	:	Liquified Petroleum Gas
Ltd.	:	Limited
Max.	:	Maximum
Min.	:	Minimum
min.	:	*minute*
Mol. wt.	:	Molecular weight
ND	:	Not Detected
nd	:	not determined
Nig.	:	Nigeria
Temp.	:	Temperature
XRD	:	X-Ray Diffraction

LIST OF NOTATIONS

M	Molecular weight, g/g-mol
mV	millivolt
N	Normality
Na	Concentration of acid, N
Nb	Concentration of base, N
na	number of moles of acid
nb	number of moles of base
P	Pressure, atm.
R	Gas constant, l. atm. /g-mol (K)
T	Temperature, K
V	Volume, ml
Va	Volume of acid, ml
Vb	Volume of base, ml
α	alpha
β	beta

CHAPTER ONE

1.0 INTRODUCTION

Sialons are ceramics composed mainly of silicon, aluminium, oxygen and nitrogen. Simplistically, they can be thought of as a hybrid of silicon nitride and alumina. They are solid solutions in the Si-Al-O-N system and the chemical symbol of the elements constitute the name for these materials. A wide range of solid solutions with α- and β-silicon nitride structure are well recognised under the name of α- and β-sialons. Sialons exhibit the hardness and thermal shock resistance of silicon nitride, offer better chemical stability and are sinterable almost up to theoretical density; an important characteristic in ceramic technology[1,2,3,4].

The first member of the class to be characterised was a nitride oxide now known as β-sialon, containing Al, Si, N and O. The compositional range for β-sialon can be expressed by a general formula: $Si_{6-Z}\ Al_Z\ O_Z\ N_{8-Z}$, where Z varies from 0 to 4[1,2,3].

A common method for the preparation of sialons is reaction sintering. Starting with the mixture of fine powdered silicon nitride, aluminium nitride, and alumina or silica, β-sialon or silicon oxynitride can be synthesized through the solid state, high temperature reaction. An addition of some other oxides, such as Yttria, Calcia, Magnesia, or Lithia can lead to a solid solution with α-silicon nitride structure; α-sialons[1,2,4].

A new but promising method for the preparation of sialons is from the naturally occurring aluminosilicate minerals; Kaolinite, Illite, Montmorillonite, etc. by carbothermal reduction and nitridation at high temperatures($\geq 1100^0C$)[1,2]. Carbothermal reduction is of interest in this work because of the availability of cheap

raw materials. It is possible to prepare many different nitrogen containing phases from Kaolinite by varying the starting composition and reaction conditions. β-sialon can be prepared by carbothermal reduction and nitridation of Kaolinitic clays at high temperatures. The resulting powders are then suitable for subsequent consolidation and use in a number of applications; from refractories for metal refining to engineering components[1,2,3,6].

Refractories form one of the most important classes of ceramic products in large use in Nigeria; refractory materials are being used by burnt bricks industries, chemical and process industries, glass plants and metallurgical industries for the construction and maintenance of kilns, furnaces, reactor vessels and boilers etc[7].

With the development of Iron and Steel industries in Nigeria the demand for refractory materials which are still being imported is increasing. For example, Delta Steel Company, Jos Steel Rolling Mill, Katsina Steel Rolling Mill and other metallurgical plants in the country still import their refractory materials. The Ajaokuta Steel complex on completion will require about 36,000 tonnes of refractory bricks for relining purposes[7]. To reduce this dependence on foreign refractory materials, the abundant deposits of Kaolinitic clays in the country can be properly exploited in the production of refractory articles including β-sialon based materials, to meet these demands and for export.

The preparation of β-sialon powder from naturally occurring raw materials such as Kaolinitic clays by simultaneous carbothermal reduction and nitridation, offers an economically attractive production route. The reducing agent commonly employed is carbon. Although metallic aluminium powders can be used instead, but coal which is a cheap source of carbon is readily available and much cheaper than metallic aluminium. The nitridation reaction occurs in nitrogen atmosphere. Kaolinitic or Halloysitic clays are the natural raw materials mostly used; they are probably the most

suitable to be employed in the nitridation process[1,2]. Hence this investigation is aimed at producing β -sialon from Kankara clay, a good local kaolin by carbothermal reduction. Onyeama coal would be used as the source of carbon for the reduction reaction. The reaction would be carried out in a nitrogen atmosphere at high temperatures using a locally assembled production facility.

In this report, literature on sialons and local raw materials are first reviewed. The fabrication and development of the reaction chamber (saggar) to be used for the high temperature preparation and the furnace assembly are next presented. The experimental procedures are then described followed by the results of the experimentation and their discussion. Conclusions and recommendations are finally made.

CHAPTER TWO

2.0 LITERATURE SURVEY

This chapter discusses sialons and their chemical composition, properties, uses and applications, and their methods of production. Literature on various raw materials for the production of sialon powders are also presented.

2.1 SIALONS AND THEIR CHEMICAL COMPOSITIONS

A wide range of solid solutions in the Si-Al-O-N system with the α and β-silicon nitride structure are well - recognised under the name of α- and β-sialons. They comprise both crystalline and glass types, containing structural silicon, aluminium, oxygen and nitrogen and an additional or alternative elements (Y, Mg, Ca, Li, etc). The first member to be characterised was a nitride - oxide now known as β-sialon, with crystal structure similar to that of β-silicon nitride[1,2,3]. The compositions developed so far exhibit the low thermal coefficient of expansion of silicon nitride but have increased oxidation resistance[1,2].

Sialons are solid solutions in the Si- Al- O- N system and the chemical symbols of the elements constitute the name of these materials. The binary compounds in the system are silicon nitride (Si_3N_4), silicon oxide (SiO_2), aluminium nitride (AlN), and aluminium oxide (Al_2O_3); so the system can be represented also by adopting these simple compounds as extreme terms. As represented in the most used phase diagram (Figure 1), there are a lot of different stable compounds at a given temperature, but β-sialons are the most interesting ones[1,2,4].

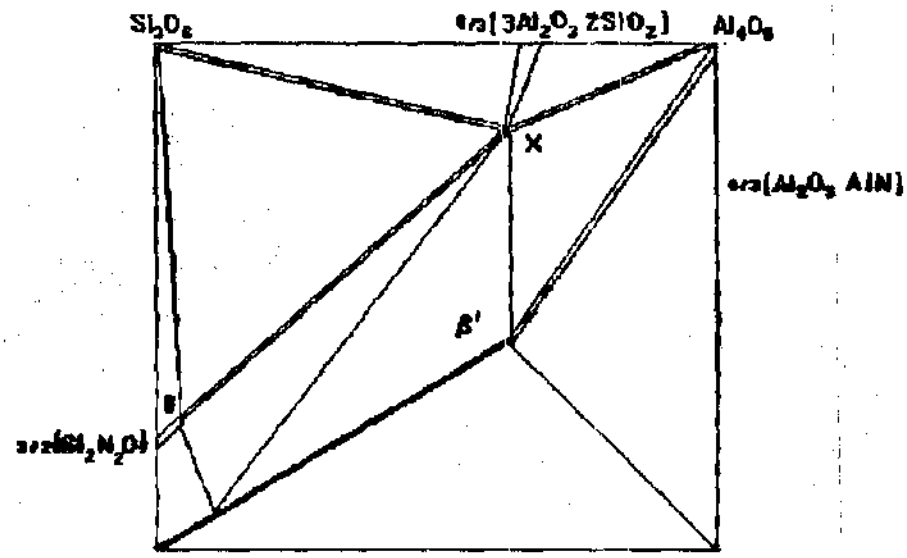


Figure 1 The Si - Al - O - N System at 1400^{0}C (after Jack)[1,2,3,4]

These compounds have structure similar to that of silicon nitride β-phase; this is built up of $(Si,Al)(O,N)_4$ tetrahedra in the same way that the structural units of silicates are SiO_4 tetrahedra. The substitution of a tetravalent silicon cation by a trivalent aluminium one needs a correspondent substitution of trivalent nitrogen by bivalent oxygen. Thus sialons may be regarded as silicon nitrides containing substitutional aluminium and oxygen. Structurally and as materials, they are similar to and may be indistinguishable from dense silicon nitride[1,2,3].
The compositional range for β-sialon can be expressed by the general formula;

$$Si_{6-z}Al_zO_zN_{8-z}$$

The solid solution is stable in the compositional range with z about from 0 to 4. This is the principal compound obtained when clayey raw materials are used to produce sialon powders[1,2].

2.2 ENGINEERING PROPERTIES

Sialons have a wide range of engineering properties which make it suitable for use in many engineering applications. Tensile strength of 1 to 1.5 GPa and toughness value of 8 to 10 MPa . $m^{1/2}$ are the outstanding properties of sialons[3,4,5]. They are shaped in the green state and require only minimal diamond machining to allow precision fitting[1].

Typical properties of sialons are as listed in Table 1[3,4,5].

Table 1 Typical properties of sialons

Density, kg/m^3	3200
Hardness, GPa	18
Toughness, $MPa \cdot m^{1/2}$	8 to 10
Young Modulus, GPa	440
Tensile Strength at 25°C, MPa	1000 to 1500
Thermal Expansion Coeff. , /°C	$3 * 10^{-6}$

Their mechanical strength is the most important characteristic for use as structural components at high operating temperatures. The bending strength generally increases as oxygen content decreases and its absolute value is not much less than that of silicon nitride or silicon carbide. Creep resistance and thermal shock resistances are better for sialons than for silicon nitride, and the hardness is comparable with that of the conventional materials (tungsten carbide, alumina) used for cutting of extruded metals. The oxidation resistance of sialons is better than that of silicon nitride; from this point of view , probably because a protective oxidised layer of mullite is formed on the surface. Sialons have high resistance to chemical attack by molten metals. They are sinterable almost up to theoretical density[1,2,3].

2.3 APPLICATIONS

Ceramic materials based on the Si- Al - O - N system are potential candidates for many special ergineering applications, such as refractory articles for use in the Iron and Steel industries, Chemical and process industries, structural parts of internal combustion engines - where high strength, wear resistance and refractoriness are required, cutting tools for metal machining- since hardness and wear resistance guarantee a high working speed.

The same characteristics render these ceramic materials particularly suitable for the production of dies and other components for extrusion machines (moulds, pipes, guides etc.). The resistance to chemical attack lets different metals (copper, brass, bronze, aluminium, titanium etc.) to be satisfactorily treated[1,2]. Both, Anglo-Saxon and Japanese companies produced β-sialon based components for car-engines: pre-combustion chambers, injectors and valves; these components showed a longer durability due to the high wear resistance of sialons. However other applications of β-sialon ceramics are only in the planning state: engine components for gas turbines, elements for handling and conveying fused metals, cutting tools for rock articles and components for ball bearings. Potential uses of β-sialon in Nigeria are mainly as a refractory material for use in the Iron and Steel industries, chemical and process industries, glass plants and other non-ferrous metallurgical industries[1,2,3,6].

2.4 β-SIALON POWDERS FROM NATURAL RAW MATERIALS

Sialon powders from natural raw materials are prepared by means of a reduction reaction and nitridation process at high temperatures (≥ 1100°C). Reducing agent is commonly represented by carbon - carbothermal reduction, or infrequently by metallic aluminium powders. Nitridation is possible since the reaction occurs in nitrogen or ammonia atmosphere[1,2].

2.4.1 Carbothermal reduction of natural silicatic raw materials

The carbothermal reaction is a reduction and nitridation process frequently used in the preparation of sialon powders from natural silicatic materials. Lee and Cutler were the first to describe the reaction of clay - carbon mixture with nitrogen to obtain β-sialon, $Si_3Al_3O_3N_5$[1,2,3]. Obviously all the different materials used are constituted principally of silica and alumina, since silicon and

aluminium are the only cations contained in the theoretical formula of β-sialon as can be seen in Figure 2[1,2]

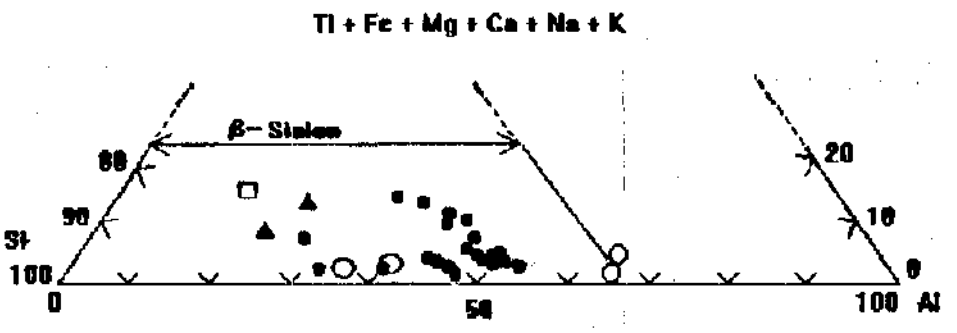


Figure 2 Ternary representation Si-Al-(Tl + Fe + Mg + Ca + Na + K) at the molar composition for the diferent natural materials used to obtain β-sialon powders by carbothermal reduction: kaolins and kaolinitic clays (black circles); illitic and montmorillonic clays (triangles); pyrophillytic materials (empty circles); sillimanite and similar materials (hexagons); volcanic glass (square). [1]

The process consists fundamentally of the reduction of silica and alumina by free carbon at high temperatures(1100 - 1500^{0}C) for some hours. At the same time nitridation occurs by partial removal of oxygen as gaseous carbon monoxide or H_2O in nitrogen rather than nitrogen/hydrogen or ammonia atmosphere. The progress of the reaction or the formation of β-sialon can thus be monitored by following the concentration of carbon monoxide . Other than purified coal, organic polymers, graphite, or waste materials such as rice hulls may be used as carbon sources.

2.4.1.1 Carbothermal Reduction of Kaolinitic Clays

Kaolins and Kaolinitic or halloysitic clays are the natural raw materials used and probably the most suitable to be employed in the nitridation process. The use of kaolin as starting materials for the production of sialon powders was first proposed by Wild in 1976, but the carbothermal reduction processing of clays with high kaolinite and/or halloysite content has been intensively studied after Lee and Cutler in 1979[1,2,6].
Theoretically the reaction takes place as follows:

$$3(2SiO_2 \cdot Al_2O_3 \cdot 2H_2O)_{(s)} + 15C_{(s)} + 5N_{2\,(g)} \longrightarrow$$
$$\longrightarrow 2Si_3Al_3O_3N_{5\,(s)} + 15CO_{(g)} + 6H_2O_{(g)} \qquad (2.1)$$

The final result being a β-sialon phase with Z=3 in its formula. Thus Kaolinite, which has an Al:Si atom ratio of 1:1, can be used to prepare β-sialon of Z = 3. The reaction is thermodynamically favourable but the reaction mechanism depends on other factors and in particular on the role of impurities present in the clay and carbon. These impurities are frequently inherited into the sialon powder and then may play a role in subsequent sintering to form dense components[6].

Practically the reaction develops in several stages, with formation of intermediate phases. According to Higgins and Hendry the reaction kinetics show three main steps[1,2]:

(i) thermal decomposition of kaolinite to mullite and free silica;

(2) reduction of free silica to silicon carbide;

(3) reaction of carbon, silicon carbide and mullite with nitrogen gas to give β-sialon.

The behavior of kaolinite on heating is documented . At about 500°C, dehydration occurs giving amorphous material (meta-kaolin) and at 1200°C nucleation of mullite occurs. At the reaction temperature, 1400°C, the kaolinite is therefore already broken down into a mixture of mullite and free silica[1,2];

$$\underset{\text{kaolinite}}{3(2SiO_2 \cdot Al_2O_3 \cdot 2H_2O)} \longrightarrow \underset{\text{mullite}}{3Al_2O_3 \cdot 2SiO_2} + \underset{\text{free silica}}{4SiO_2} + 6H_2O \qquad (2.2)$$

and the reactants are in the form of a mixture of crystalline mullite and amorphous silica and carbon. During heating the coal has given off all volatile matter and at reaction temperature is impure, amorphous carbon[2].

The second stage is the reduction of free silica to silicon carbide.

$$4SiO_2 + 12C \longrightarrow 4SiC + 8CO \qquad (2.3)$$

and the third stage is the isothermal formation of β-sialon;

$$3Al_2O_3 \cdot 2SiO_2 + 4SiC + 3C + 5N_2 \longrightarrow \underset{\beta\text{-Sialon}}{2Si_3Al_3O_3N_5} + 7CO \qquad (2.4)$$

Pyrophilitic processing at 1320 - 1420^{0}C produced powders constituted mainly of β-sialon, containing some traces of silicon oxynitride, α-sialon, β-SiC and β-silicon nitride or mullite corundum. A value of Z = 0.8 for the β-sialon phase has been reported[2].

2.4.1.4 Other aluminosilicate materials

Literature on the carbothermal processing of various other aluminosilicatic materials is very scanty, such as volcanic glass, zeolite and sillimanite. Sialon powders from sillimanite have indeed been obtained only by Mukerji et al[10], since Baldo et al used two mixes appropriately prepared to approach the composition of sillimanite.

Carbothermal reduction has been realised at 1300 - 1500^{0}C, given rise to β-sialon, as main component, and small quantities of both oxides and nitride (or carbide) compounds[1,2].

2.4.1.5 Magnesium silicates

Sialon and silicon nitride powders have been experimentally produced also by nitriding different natural magnesium silicates, such as sepiolite, antigorite, hectorite, vermiculite and saponite. In the case of both sepiolite and antigorite carbothermal reduction at 1400 - 1500^{0}C leads to β-Si_3N_4 prevailing on $MgSiN_2$, forsterite and traces of other compounds[1,2].

2.4.2 Reduction by Aluminium

The nitridation processing of natural raw materials has been performed also in different ways as to the carbothermal reduction; using metallic aluminium powder as reducing agent in nitrogen atmosphere. In this case the reducing agent also constitutes the aluminium source of β-sialon, so that the process can be applied

to quartziferous raw materials other than volcanic glass.

Nitridation occurs at 1300 - 1500^{0}C leading to the formation of β-sialon prevailing over accessory phases such as AlN, α-Al_2O_3, SiC, Al and silicon oxynitride, and unreacted silica and aluminium. The β-sialon composition ranges widely according to the ratio between the amounts of the starting silica and added aluminium[1,2].

CHAPTER THREE

3.0 EQUIPMENT, MATERIALS AND INSTRUMENTATION

This chapter presents the lists of equipment, materials and reagents including instrumentation where necessary, employed in this study. Full description of the furnace assembly and fabrication of the saggar to be used for the high temperature reaction are presented in the next chapter.

3.1 BENEFICIATION OF KANKARA CLAY

The equipment used in the beneficiation of Kankara clay are as follows;

(1) Biscuit-fired clay pots
(2) Tyler mesh sieve (75μm)
(3) Porcelain mortar and Pestle
(4) Oven (Gallenkamp, model OV - 240)

3.2 PULVERIZATION OF ONYEAMA COAL

The equipment employed in the pulverization of Onyeama Coal include;

(1) Jaw crusher (Pascall Eng. Co. Ltd. Sussex, model no. 17769)
(2) Grinder (Pascall Eng. Co. Ltd. Sussex, model no. 17834)
(3) Sieve shaker (Pascall Eng. Co. Ltd. Sussex, model no. 17747)
(4) Tyler mesh sieves (75, 180, and 250 μm)

3.3 CLAY - COAL MIXING

The equipment used in mixing the various proportions of Kankara clay and Onyeama Coal are as follows;

(1) Ball mill with porcelain pot
(2) Tyler mesh sieve (75 μm)
(3) Sieve shaker
(4) Porcelain crucibles
(5) Weighing balance
(6) Glass Desiccator
(7) Oven (Gallenkamp, model OV - 240)
(8) Sampling bottles
(9) Stainless steel spatula

3.4 PROXIMATE ANALYSIS OF ONYEAMA COAL

The equipment used in carrying out proximate analysis of the Onyeama Coal include;

(1) Heraeus Furnace (Zoetermeter, Holland, 100 - 1400^{0}C)
(2) Porcelain crucibles
(3) Silica crucibles
(4) Weighing balance

3.5 FABRICATION OF THE SAGGAR

The equipment and materials employed in the fabrication of the saggar include the following;

(1) Kankara Grog
(2) High Alumina Refractory cement
(3) Water
(4) Porcelain Mortar
(5) Paraffin Wax

(6) Cardboard paper
(7) Plastic Measuring Cylinder
(8) Hot plate
(9) Oven (Gallenkamp, model OV-240)
(10) Porcelain Crucibles
(11) Crucible Tongs
(12) Weighing balance
(13) Metal Kettle

3.6 FURNACE ASSEMBLY

The equipment and materials employed in the furnace assembly are as follows;

(1) Galvanised Iron Sheet
(2) Angled Iron
(3) Refractory cement
(4) Diatomite
(5) Kankara Grog
(6) Insulation bricks
(7) Welding Machine
(8) Welding electrodes
(9) Tape Rule
(10) Roller machine
(11) Hack saw
(12) Vice

3.7 THERMAL TREATMENT OF CLAY - COAL MIXTURE

The equipment employed in the thermal treatment of the clay - coal mixture are as follows;

(1) Gas fired furnace
(2) Reaction chamber - saggar
(3) Thermocouple

(4) LPG bottles
(5) Nitrogen gas
(6) Chart recorder
(7) Blower
(8) Rotameter

Figure 3 shows the set up of the experimental rig.

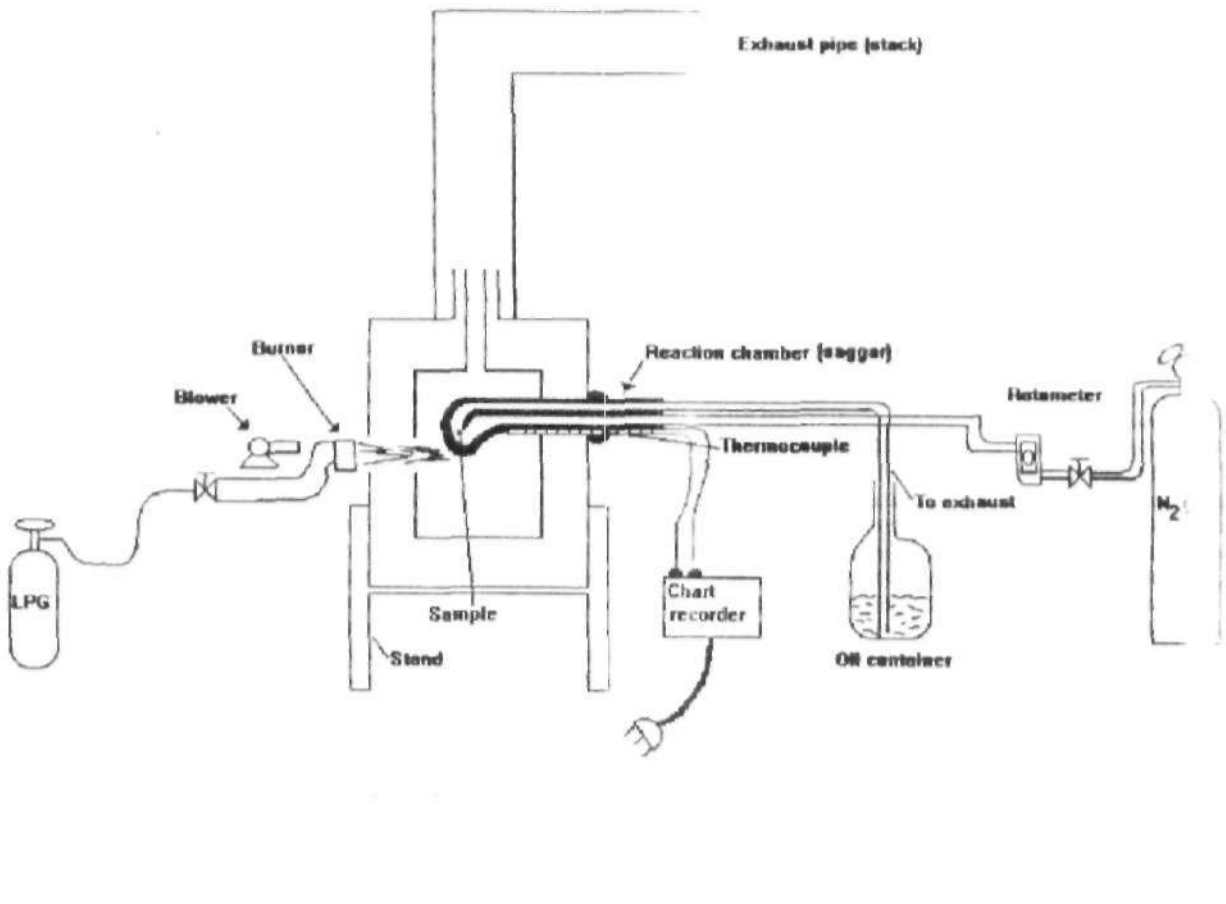


Figure 3 The Diagram of the experimental set-up

3.9.2 Apparatus and Equipment

(1) Burette (10 ml, 20 ml)
(2) Pipette (10 ml, 20 ml)
(3) Standard flask (1 l)
(4) Distillation flask (800 ml)
(5) Round bottom flask (500 ml)
(6) Conical flask (100, 250, 500 ml)
(7) Measuring cylinder
(8) Glass beakers (100,400, 500 ml)
(9) Bunsen burner
(10) Kjeldahl distillation apparatus

CHAPTER FOUR

4.0 EXPERIMENTAL PROCEDURE

This chapter describes the methodology involved in the laboratory production of β-sialon using locally available raw materials. The preparation of raw materials, fabrication of reaction chamber, furnace assembly, thermal treatment of reactants, analysis of exit gases from the reaction chamber, nitrogen analysis of the sialon product obtained and calibration of rotameter are also presented.

4.1 APPROACH

Carbothermal reduction of Kankara clay, which is predominantly kaolinitic in nature, and locally available and cheap has been employed for the production of β-sialon. The reaction has been carried out using a locally manufactured gas fired furnace and a locally fabricated reaction chamber. The source of the carbon that is required for the reduction reaction is the Onyeama coal. Nitrogen gas which is about 79% of the atmospheric air was procured from the Industrial Gases (Nig.) Limited, for the nitriding process. Figure 4 gives a block diagram of the various process stages involved in the laboratory production of β-sialon powder from these materials.

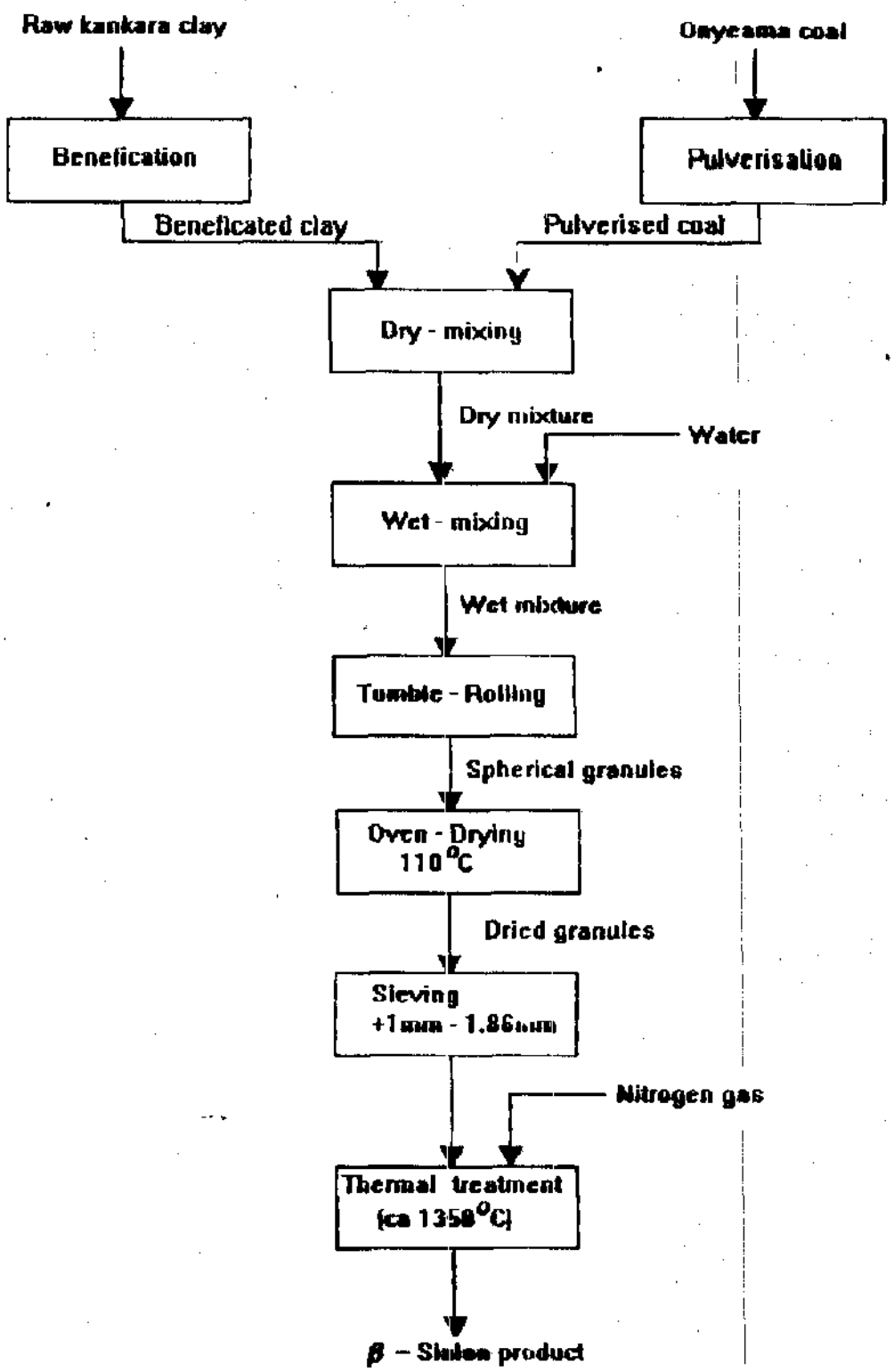


Figure 4 Process stages for the production of β-sialon

4.2 PREPARATION OF RAW MATERIALS

4.2.1 Beneficiation of Kankara Clay

Kankara clay was beneficiated by screening through tyler sieve of 200 mesh size (75μm). The clay lumps were first slaked by soaking in water for overnight. The resultant slurry was screened through the sieve (75μm). The sieved clay suspension was dewatered in biscuit-fired clay pot for 48 hours and was broken into sizeable fragments. The fragments were dried first in ambient air for 72 hours and then in a Gallenkamp Oven, model OV - 420, at 110^0C for 24 hours. Figure 5 shows the flow diagram of the operations carried out.

4.2.2 Pulverization of Onyeama Coal

Onyeama coal which is locally available was chosen to be the source of carbon for the reduction reaction. The sample of the coal was obtained from the Department of Mineral Resources Engineering of Kaduna Polytechnic, Kaduna in lump form . The lumps were first crushed using a jaw crusher and ground using a grinding machine (Pascall Engineering Co. Sussex). The ground coal was then sieved through tyler sieve of 250μm sieve opening. The coal was then kept ready for proximate analysis.

4.2.3 Proximate Analysis

The proximate analysis is the analytical procedure followed in the assessment of the quality and type of coal. Parameters determined include; moisture content, volatile matter, fixed carbon (by difference), and ash content of coal sample.

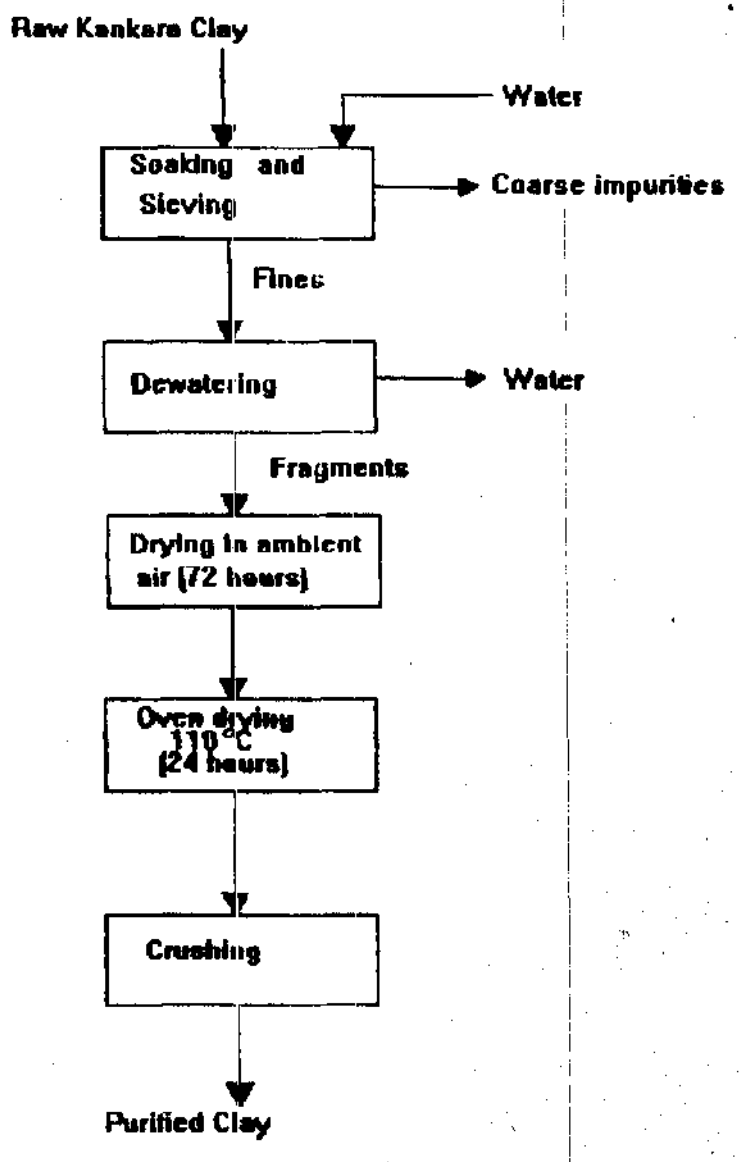


Figure 5 Beneficiation stages for Kankara clay

4.2.3.1 Determination of moisture content

Moisture is essentially water, which can be quantitatively determined by definite prescribed methods which may vary according to the nature of material. The ASTM D3173 method was employed in the determination of moisture content of the Onyeama coal sample[11].

4.2.3.2 Determination of ash

Ash with reference to coal and coke is defined as the inorganic residue remaining after complete combustion of combustible substances, under strictly controlled conditions. ASTM D3174 method was employed in the determination of ash content of the Onyeama coal sample[11].

4.2.3.3 Determination of volatile matter

Volatile matter are those products, exclusive of moisture, given off by a material as gas or vapour, determined by definite prescribed methods, which may vary according to the nature of the material. ASTM D3175 method was employed for the determination of volatile matter in the Onyeama coal sample[11].

4.2.3.4 Determination of fixed carbon

Fixed carbon in the case of coal or coke and bituminous materials, is the solid residue other than ash obtained by destructive distillation by definite prescribed methods. However, proximate analysis was carried out on the coal sample and hence the amount of fixed carbon was obtained by difference as[11];

Fixed carbon = 100 - (volatile less moisture + moisture + ash)

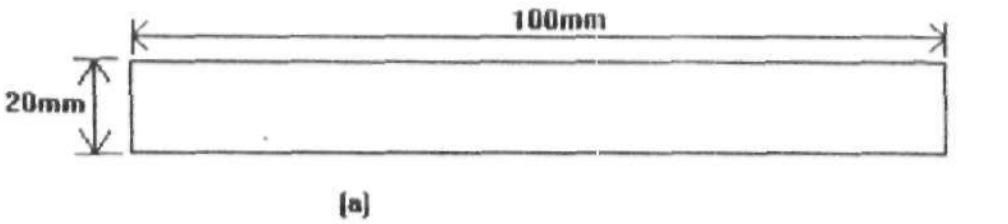
4.3 MIXING OF RAW MATERIALS

The beneficiated clay and the pulverized coal were dry-mixed in proportion according to the thecretical reaction equation for the production of β-sialon (see Appendix A for mix calculations). The mixing was carried out using a ball mill for four hours and thereafter water was added to dampen the mixture. The dampen powder of the mixture was then tumble-rolled for a period of 30 minutes in a milling machine to obtain spherical granules. The granules were dried in a Gallenkamp oven at 110^{0}C for six hours. The granules were then sieved to a size fraction between 1 mm and 1.86 mm (the available sieves). The sieved granules were placed in sampling bottles and kept ready for thermal treatment.

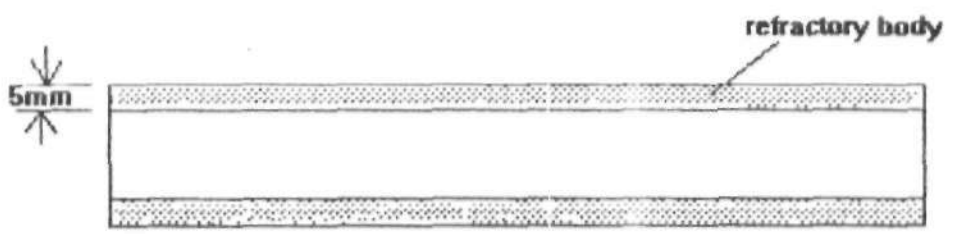
4.4 FABRICATION OF THE REACTION CHAMBER (SAGGAR)

The reaction to produce β-sialon from mixtures of kaolinite and coal was carried out under a reducing atmosphere. A reaction chamber was therefore designed and fabricated using investment casting technique to enable a reducing atmosphere condition to be created for the carbothermal reduction and nitridation process. The saggar was designed to allow the passage of nitrogen gas to exclude oxygen as well as to serve as the reactant gas.

Test pieces were first tried from various mix proportions of Kankara clay and a high alumina refractory cement. Paraffin wax rods of approximately 20 mm in diameter and 100 mm long were used. Various body compositions were then tried on the wax. This was done by plastering the body onto the wax rods to a thickness of about 5mm as shown in Figure 6.



(a)



(b)

Figure 6 Test piece of paraffin wax castable: (a) Paraffin wax mould, (b) section of plastered paraffin wax

The test pieces were allowed to dry at an ambient condition for 72 hours. It was then transferred to the Gallenkamp oven so that the wax could melt away (from room temperature, 28^{0}C to 60^{0}C) for 12 hours. The oven was then allowed to cool down for another six hours. The test pieces were removed from the oven and visually observed for cracks.The test pieces with least cracks containing 10% refractory cement and 90% Kankara grog was chosen for the fabrication of the saggar.

The saggar was designed so that it conforms to the available space in the firing port of an existing furnace design. It has an inlet and outlet and a reaction zone. The inlet allows nitrogen gas to flow through to the reaction zone, where the clay - coal mixture (the spherical granules) were placed, while the outlet allows the exit gases from the reaction chamber (saggar) to flow out. The reaction zone was obtained by carving out the shape from a solid paraffin wax of cylindrical shape as shown in Figure 7.

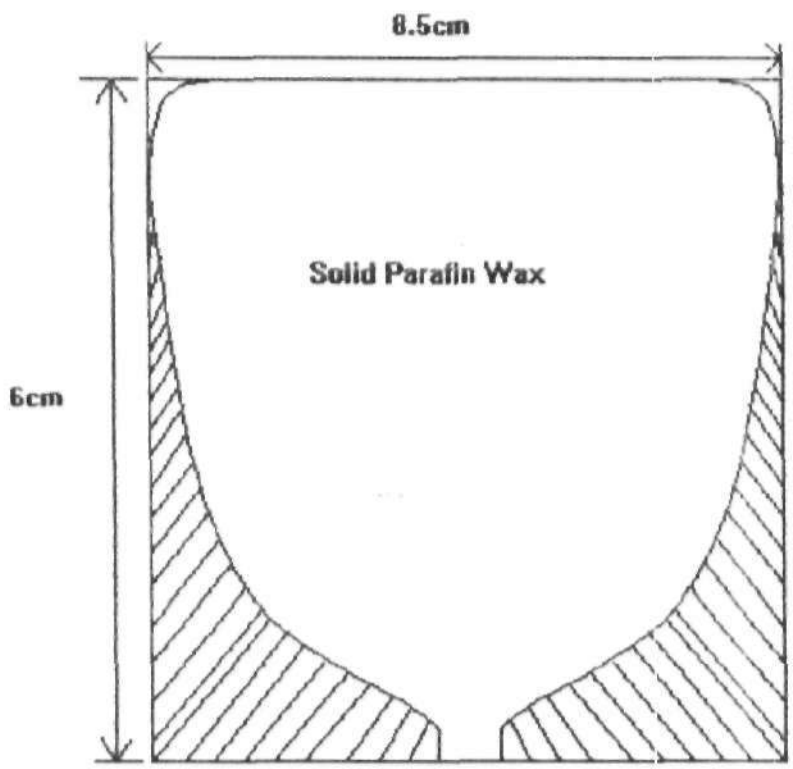


Figure 7 Parafin Wax mould of the reaction zone

The inlet and the out let of the saggar were also fabricated using the paraffin wax. A cardboard paper was folded to give a desired cylindrical shape of 10 mm in diameter and 300 mm long. Melted paraffin wax was then poured into the hole of the folded cardboard and then allowed to cool and solidify. After solidification, the cardboard was then removed leaving the wax as in Figure 8.

Appropriate connections of Figures 7 and 8 were carried out by melting the wax and manipulations using heat to obtain the required shape as shown in Figure 9.

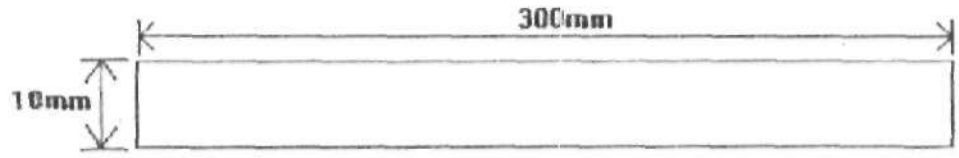


Figure 8 Parafin wax mould of the inlet and outlet of the saggar

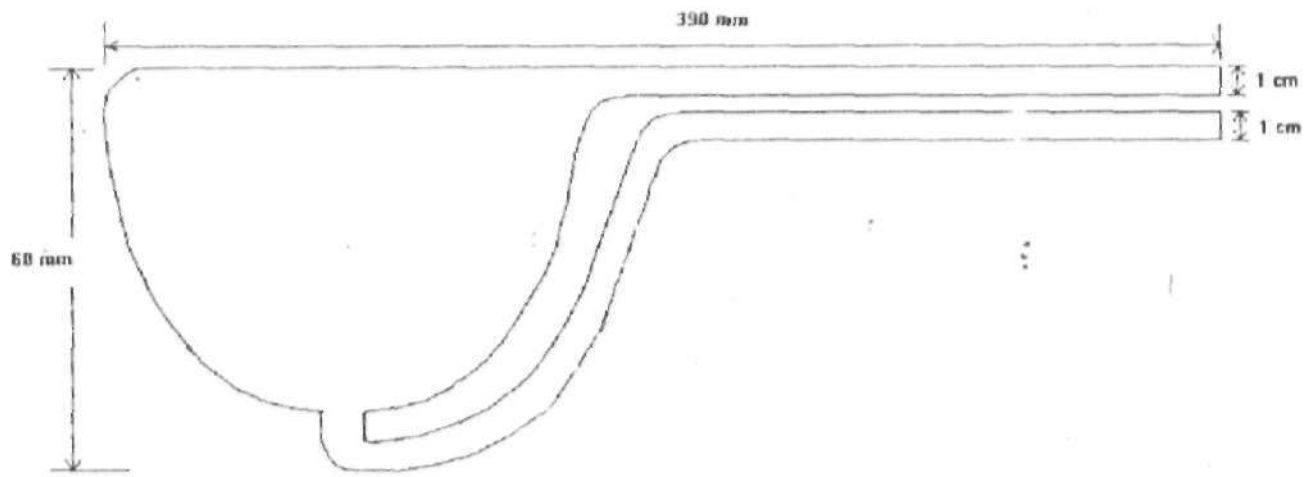


Figure 9 Paraffin wax shape of the saggar

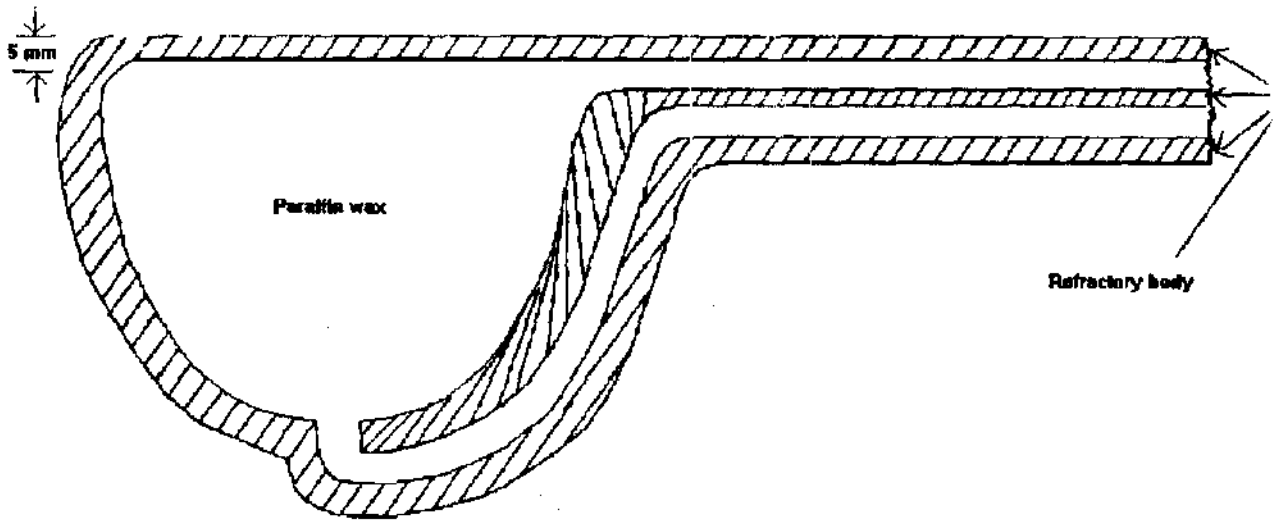


Figure 10 Plastered paraffin wax mould of the saggar

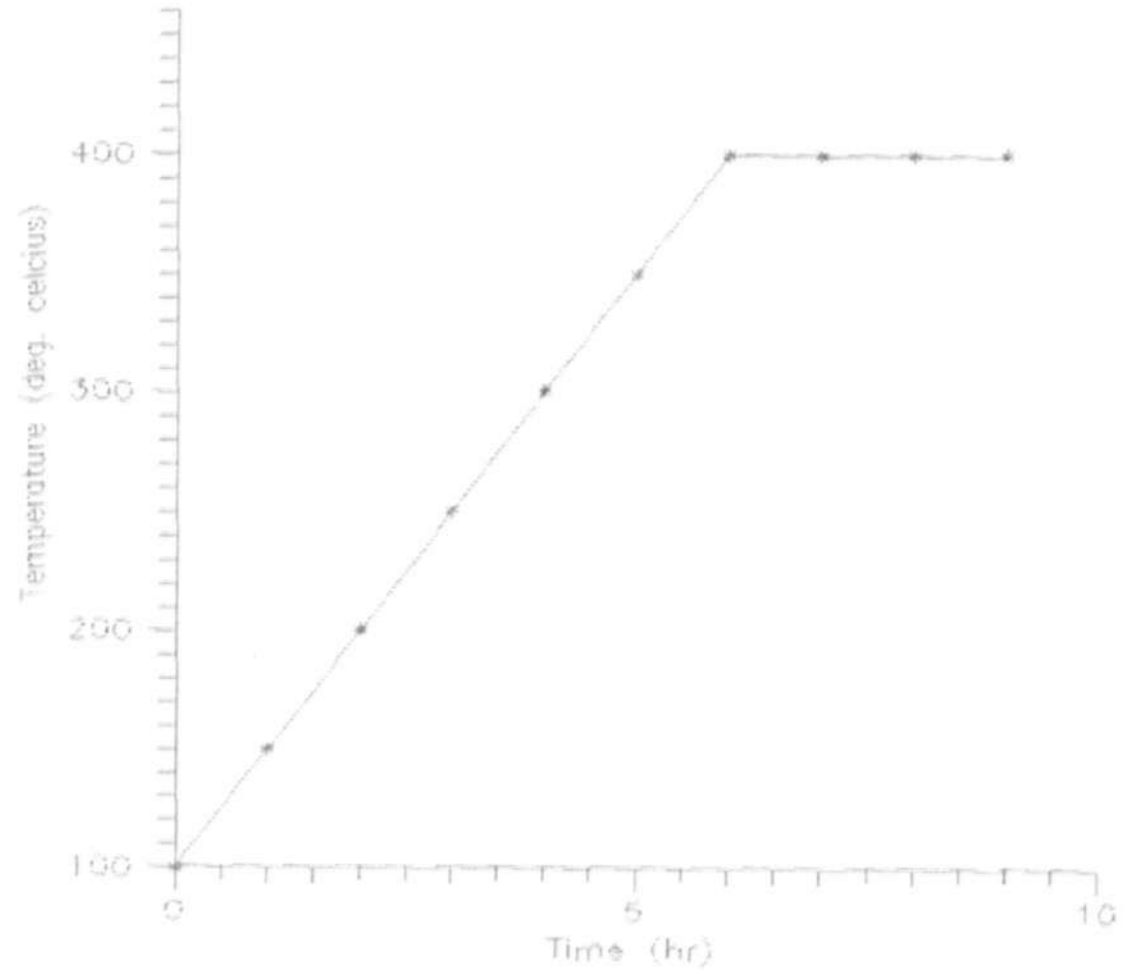


Figure 11 Pre-firing schedule for the Saggars

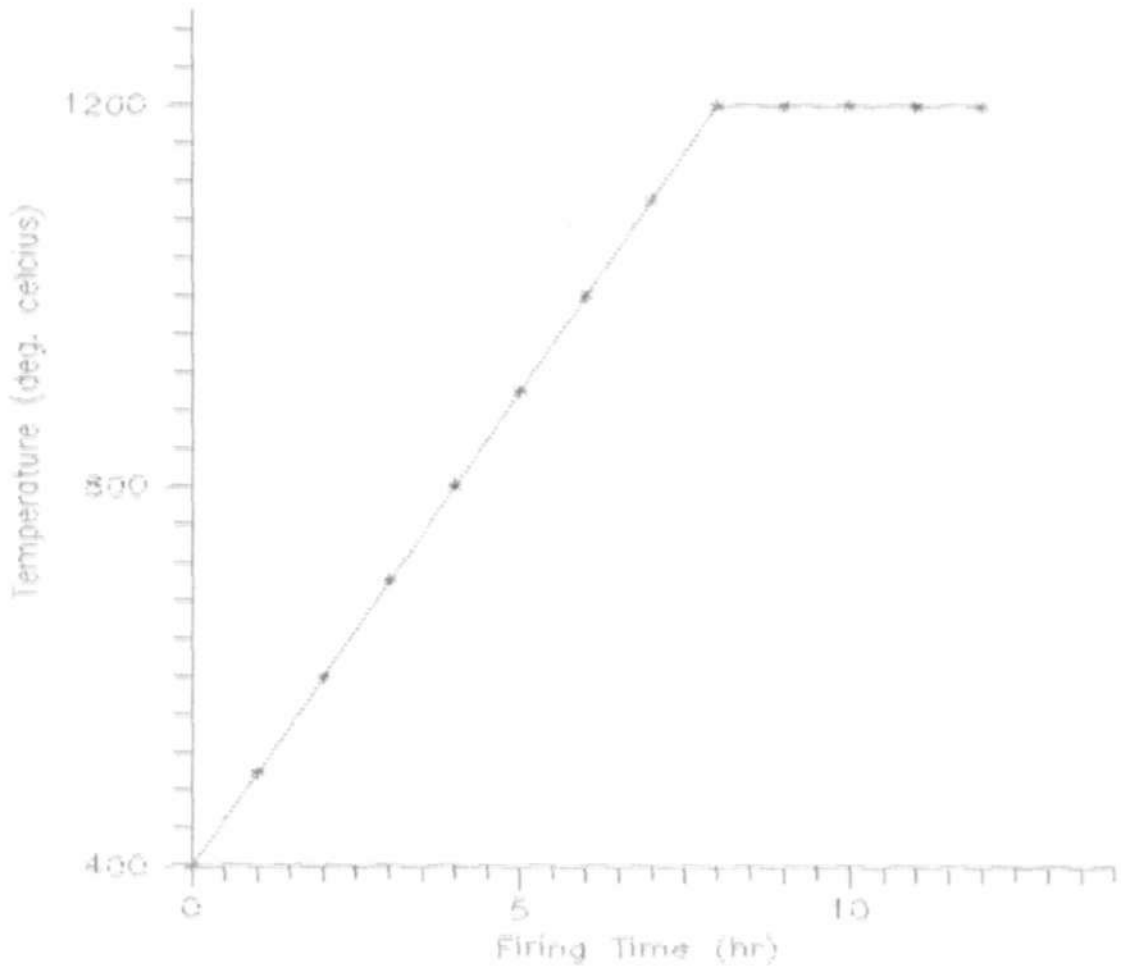


Figure 12 Firing schedule for the Saggars

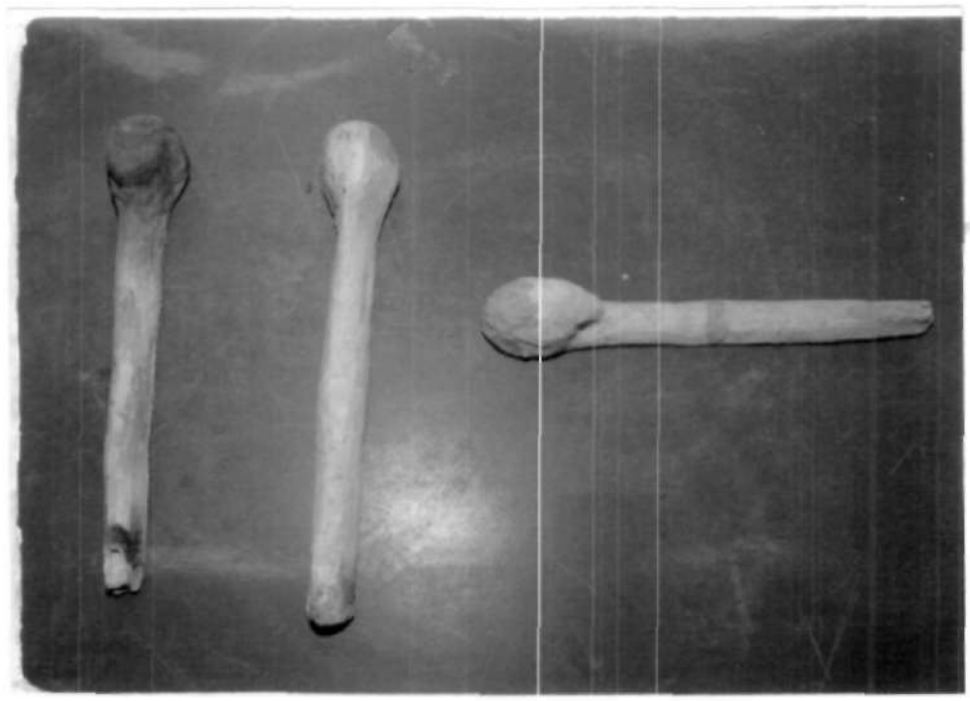


Plate 1 Saggars fabricated for the high temperature reaction

4.5 FURNACE ASSEMBLY

An existing gas fired furnace design partially constructed was completed and assembled so that it could be used for the production of β-sialon from Kankara clay.

4.5.1 Work done on the Furnace

The following activities were effected on the furnace so that it could be used for the carbothermal reduction and nitridation of kankara clay to produce β-sialon:

(1) Construction of Stack
(2) Construction of furnace stand
(3) Providing insulation
(4) Welding and coupling of the various parts of the furnace
(5) Testing of the furnace.

4.5.1.1 Construction of the Stack

The construction of the Stack was carried out thus:

Material : - galvanised Iron sheet (16 gauge)

Dimensions: - Vertical; internal diameter ~ 0.120 m
length ~1 m

- Horizontal; internal diameter ~0.060 m
length ~0.5 m

The parts were rolled into the required circular shape using a roller machine and welded using gas welding. Plate 2 shows the Stack pipe section of the furnace as constructed.

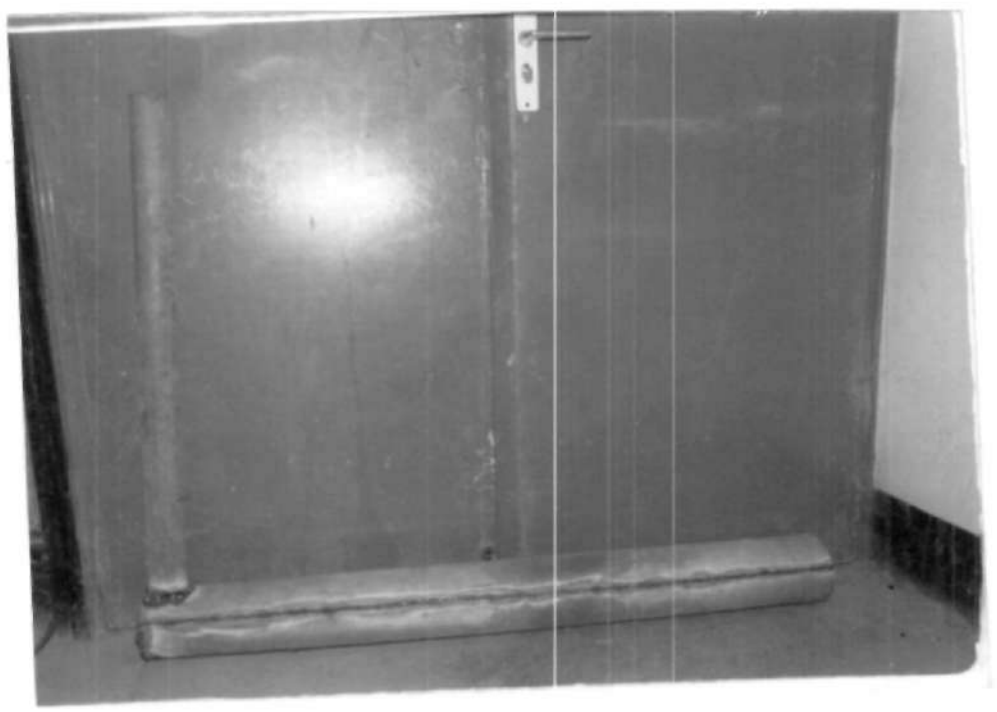


Plate 2 The stack pipe section of the assembled furnace

4.5.1.2 Furnace Stand and Support

The furnace support and stand were constructed as follows :

Material : - Angled Iron (1.5 by 1.5 cm)

Dimensions : - Legs; 0.380 m *4 = 1.52 m
- Base; 0.450 m *6 = 2.70 m

The parts were welded together using electric arc welding.

4.5.1.3 Insulation Material

The insulation for the furnace is made up of insulating bricks and diatomite. Insulating bricks were made from mix proportions of Kankara grog and saw dust. The bricks were dried in ambient air for 48 hours and further dried in oven for 24 hours. The dried bricks were fired to 1200^{0}C in the Heraeus furnace for 12 hours.The firing schedule is presented as Figure 13. The dried bricks were allowed to cool and then crushed to sizeable fragments. The insulation was then made by mixing these fragments with the already prepared diatomite. The mixture was then poured in-between the furnace wall and the metal casing.

4.5.1.4 Welding and Coupling

After filling in the insulation, the furnace was then coupled up and welded ready for testing. Figure 14 shows the diagram of the furnace whereas Plate 3 shows the assembled furnace.

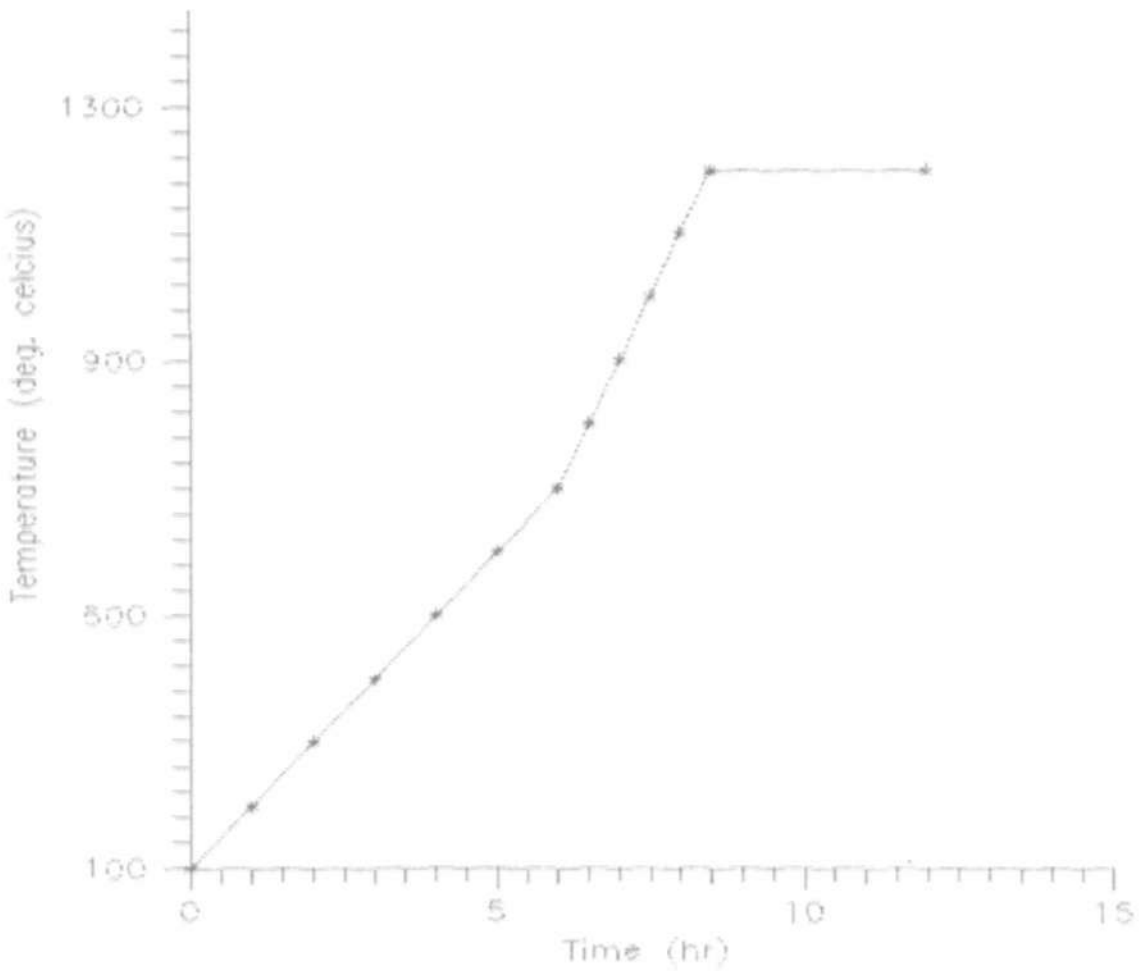


Figure 13 Firing schedule for the insulating bricks

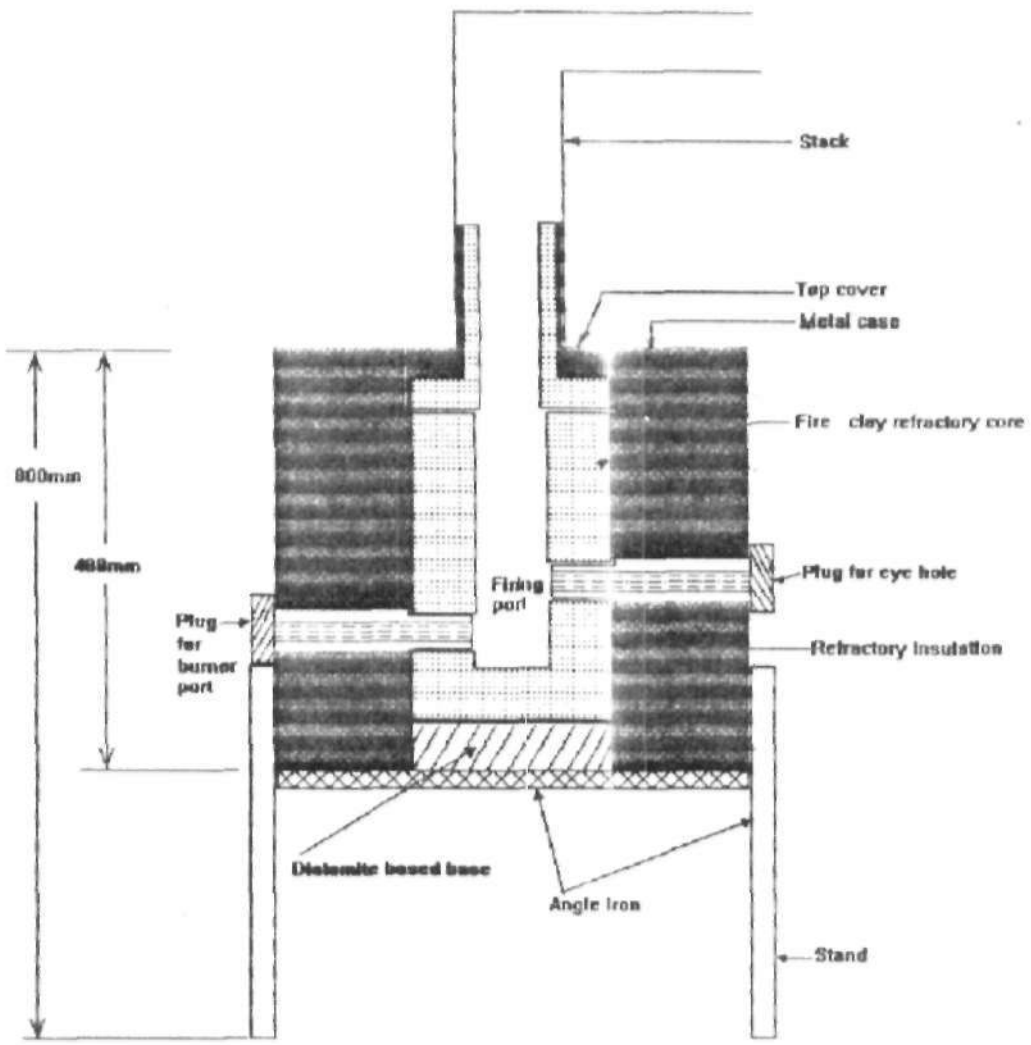


Figure 14 Cross sectional view of the gas-fired furnace



Plate 3 The assembled gas-fired furnace

4.5.2 Testing of the Furnace

The furnace so assembled was connected to the various accessories *according to Plate 4.*

LPG was supplied to a gas burner and then the firing commenced. The temperature progression was monitored by a thermocouple that was connected to a chart recorder. The thermocouple together with the chart recorder were calibrated using Heraeus furnace from 100 - 1300^{0}C. The temperature progression of the furnace was then extrapolated from the calibration curve.



Plate 4 The set-up of the experimental rig

4.6 THERMAL TREATMENT OF THE CLAY - COAL MIXTURE

4.6.1 Firing of Reactants

Three grammes of the clay - coal spherical granules were weighed into a sampling bottle and kept in a desiccator. The experimental rig was then set up.

The weighed samples were then transferred to the already fabricated reaction chamber(saggar). The saggar was placed into the furnace via the saggar port. A Chromel (K-type) thermocouple was also inserted rightly behind the saggar in the furnace. The saggar port was then sealed up using a high alumina refractory cement. Appropriate connections were made according to Plate 4 and nitrogen gas allowed to flow through the reaction chamber and then firing commenced. LPG was supplied via regulator to the burner into the firing port.

The firing continued for 12 hours for the first batch. When the firing was stopped, the nitrogen gas was allowed to continue flowing until when the temperature fell below 1000^{0}C. The furnace was allowed to cool down overnight. The cooled products were removed from the reaction chamber and placed in a sampling bottle ready for nitrogen analysis. This procedure was repeated for the other two batches at different nitrogen flowrates and firing times.

4.6.2 Temperature Monitoring

The temperature of the furnace was monitored with the aid of the Chromel thermocouple which was connected to a chart recorder. The thermocouple was prior to the firing, calibrated using a Heraeus furnace from 100 to 1300^{0}C. The temperature of the reaction was thus evaluated from the calibration curve.

4.6.3 Sampling of Gas From the Reaction Chamber

Samples of exit gas stream from the reaction chamber (saggar) were collected using used infusion liquid plastic bags. Samples were collected first at interval of one hour for two hours, and thereafter at intervals of two hours for the duration of the firing. The gas stream was allowed to fill the plastic bags of approximately a litre capacity. The bags were prior to sampling tested for leakages when filled with air. The bags together with the gas contents were corked and kept ready for orsat gas analysis.

4.7 ANALYSIS OF THE EXIT GAS STREAM FROM THE REACTION CHAMBER

Orsat analysis of the exit gas stream was carried out. Basically, the Orsat - gas apparatus consists of a glass burette graduated from 0 - 50 ml, which is immersed in a water jacket and connected at the top to a stopcock manifold made of capillary tubing. Absorption vessels (connected to each manifold at each stopcock position) contain liquid absorbents that remove one or more constituents from a gas sample. The principle involved is the measurement of the reduction in volume which occurs when individual constituents of a gas are removed separately by absorption in liquid reagents.

4.7.1 Preparation of the Apparatus

The glass components were thoroughly cleaned using distilled water and assembled. The levelling bottle was attached to the bottom of the burette with sufficient length of tubing to enable the bottle to be raised above the apparatus. The levelling bottle was filled with a confining liquid (5% v/v H_2SO_4). The apparatus was tested for leakages by filling the burette with the confining liquid. Closing the stopcock (3-way switch) and lowering the levelling bottle. On standing, the level of the confining liquid shall not fall.

The absorption vessel was charged with appropriate reagent; for carbon dioxide determination a 40% w/v potassium hydroxide solution is used, for oxygen determination, an alkaline pyrogallol is used, and for carbon monoxide determination an alkaline cuprous chloride is used.

4.7.2 Introduction of the Sample

The gas supply is connected to the 3-way switch and samples are drawn into the burette by lowering the levelling bottle. The drawn gas sample was discarded to waste by raising the levelling bottle and suitable turning of the 3 - way switch. This is repeated so many times so that the sampling line and the apparatus are free of air and full of the gas to be analysed.

The gas sample is now introduced into the burette by raising the levelling bottle and opening the 3-way switch, allowing it to draw more than 50ml of the gas and then the switch closed. The levelling bottle was now placed so that the surface of the confining liquid in it is levelled with the zero mark of the burette and by repeated momentary openings of the 3-way switch to waste, the gas was released to atmosphere until the liquid in the burette is at zero mark. The 3-way switch was then kept closed for the duration of the analysis.

4.7.3 Determination of the Gas Constituents

After the gas sample has been introduced into the apparatus, the switch to the absorption vessel was opened and the levelling bottle raised and then lowered so that after about three passes, the reagent is drawn up to the original level in the absorption vessel and then its switch closed. The position of the levelling bottle is adjusted so that the level of liquid in it coincided with that in the burette and then reading noted.This was repeated until burette reading remains constant.

Similar procedure was followed in the determination of the other gases using appropriate liquid absorbent.

4.7.4 Calculations

The percentage by volume is calculated as follows:

% volume of constituent = $V_2 - V_1$

where; V_1 = burette reading (ml) before removal of constituent
V_2 = burette reading (ml) after removal of constituent

4.8 NITROGEN ANALYSIS OF THE SIALON PRODUCT

The determination of the total nitrogen in a soil sample using Kjeldahl distillation method was adopted for use in this investigation. This is because the sialon product formed which is supposed to be analysed using x-ray diffraction method was not possible as the facilities for the x-ray were not functional and rational analysis could not be performed due to insufficient data points. However since the product formed is a clay based material and which is soil based mineral, bulk nitrogen analysis of the product using Kjeldahl distillation apparatus was instead carried out[13]. The principle involved is the digestion with sulphuric acid in the presence of a mixture of potassium sulphate, ferrous sulphate, and copper sulphate. From the ammonium salts thus formed, ammonia is distilled with sodium hydroxide and absorbed in known volume of sulphuric acid. The excess of the acid left unneutralised can be determined by titration with standard alkali using methyl red indicator.

4.8.1 Digestion

Two grams of the sialon material was transferred to a clean dried Kjeldahl flask. It was then moistened with about 2 ml of water.

The flask together with the contents was shaken well and then allowed to settle for 30 minutes. 10ml of concentrated sulphuric acid was added. Two grams of the mixture of potassium sulphate, ferrous sulphate and copper sulphate, 0.2 grams of salicylic acid and one gram of sodium thiosulphate were added[13].

The flask was heated under a bunsen flame first at low flame then gradually the flame was raised. the digestion continued until when the mixture was colourless or nearly so. The flask was then swirled well and cooled under a tap.

4.8.2 Distillation

The Kjeldahl flask was thoroughly cleaned and set up. The solution was transferred by decantation tc an 800 ml distillation flask. The contents of the first flask was thoroughly washed until free from acid. The volume was made up to 100 ml. Few pieces of glass beads were added to prevent bumping. 20 ml of 45% sodium hydroxide was added from the top and distillation was carried out receiving ammonia in a known volume of N/10 sulphuric acid. The distillation was stopped after about 2/3 has been distilled[13].

4.8.3 Titration and Calculations

The excess of the N/10 sulphuric acid left unneutralised was titrated with N/10 sodium hydroxide using methyl red indicator.

The calculations were carried out as follows;

1ml of 0.1N H_2SO_4 = 14* 0.1 * 1/1000
= 0.0014 g nitrogen

weight of sample taken for nitrogen estimation = 2 g

Volume of 0.1N H_2SO_4 taken, i.e. blank value = V_1 ml

Volume of 0.1N NaOH required for neutralising the excess of the acid = V_2 ml

Volume of 0.1N H_2SO_4 acid used up for neutralising ammonia (NH_3) = $V_1 - V_2$ ml

Nitrogen in the sample = $(V_1 - V_2)$ (0.0014) g

% nitrogen in sample = $(V_1 - V_2)$ (0.0014) (100/2).

4.9 CALIBRATION OF ROTAMETER

The nitrogen gas flow rate was monitored with the use of a rotameter connected to the flow line. The rotameter was after the experimentation calibrated using atmospheric air. Table 2 gives the results of the calibration.

Table 2 Results of Rotameter Calibration

Rotameter Reading	Time (s)	Volume of Air (ml)	Flow rate (ml/s)
1.5	54.0	2000	37.0
2.0	89.5	4000	44.7
2.5	82.0	4000	48.8
2.6	39.0	2000	51.3
2.7	73.0	4000	54.8
2.8	63.0	4000	63.5

Calibration curve was obtained by plotting the data of Table 2 using regression analysis presented as Figure 15. The regression coefficient of 0.922 was obtained.

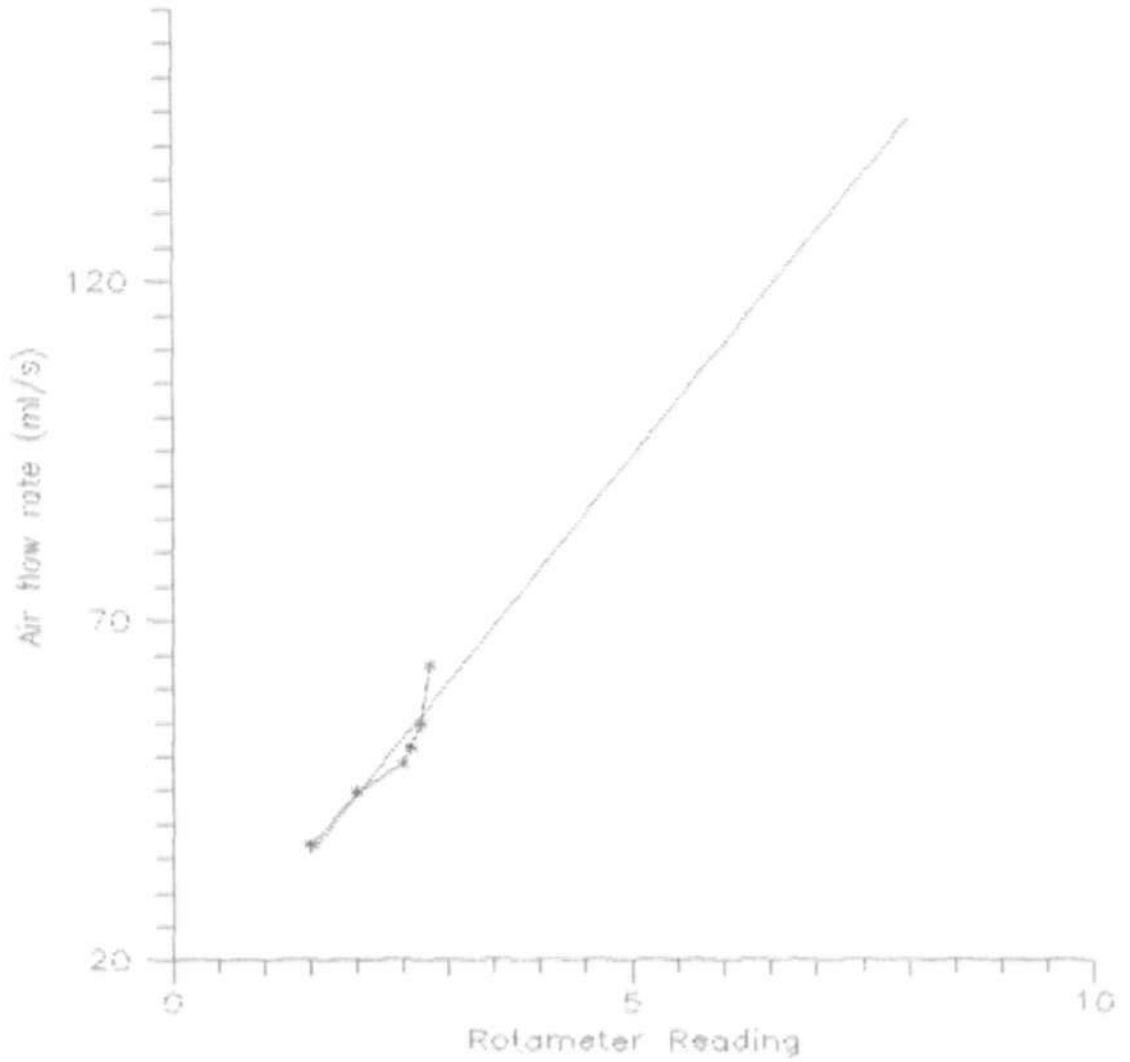


Figure 15 Best-fit Line for the Rotameter Calibration

The nitrogen gas and the air are assumed to be ideal gases at 1 atm. and 298 K[14].

Density of Air and N_2 at 1 atm. and 298 K were calculated from the following relation;

Density = M * P/R T

where, M = Mol. wt. g/g-mol
P = Pressure in atm.
T = Temperature in K
R = Gas constant = 0.08205 l . atm./g-mol . K

Density of Air = 28.96 * 1/0.08205 * 298 = 1.1844 g/l
Density of N_2 = 28.02 * 1/ 0.08205 * 298 = 1.1460 g/l

The following equation was used for the calculations of the volumetric flow rate of nitrogen gas.

$$\frac{\text{Vol.Flow rate of } N_2 * \text{Density of } N_2}{\text{Vol. Flow rate of Air * Density Air}} = \frac{\text{Mol. wt. of } N_2}{\text{Mol. wt. of Air}}$$

The air flow rates obtained from the calibration curve corresponding to the first, second and third production runs are as follows;

For the first production run the air flow rate = 72.3965 ml/s
" " second " " " " = 143.6806 ml/s
" " third " " " " = 102.2364 ml/s

The volumetric flow rate of nitrogen equivalent to the air flow rate at the same condition for the three runs were calculated from the above equation.

For the first production run,

N_2 gas flow rate = (28.02/28.96)*(1.1844/1.1460)*72.3965

= 72.3937 ml/s

For the second production run,

N_2 gas flow rate = (28.02/28.96)*(1.1844/1.1460)*143.6806

= 143.6751 ml/s

For the third production run,

N_2 gas flow rate = (28.02/28.96)*(1.1844/1.1460)*102.2364

= 102.2325 ml/s

CHAPTER FIVE

5.0 RESULTS AND DISCUSSIONS

This chapter presents the results obtained from the investigations carried out in this work.

The analysis of the Kankara clay was adopted from previous workers[7], whereas analysis on the onyeama coal was carried out in the laboratory using the American Society for Testing and Materials (ASTM D3173 -3175)[11]. From Table A2 it can be seen that kankara clay is predominantly kaolinite, 83.4 wt% for the raw clay and 91.7 wt% for the beneficiated clay (-200 mesh).

The proximate analysis as carried out on the Onyeama coal has shown the following results:

Table 3 Proximate Analysis of Onyeama Coal

Parameters	wt %
Moisture	0.09
Volatiles	8.91
Ash	5.10
Fixed Carbon	85.90
Total	100.00

From Table 3 it can be seen that Onyeama coal has about 86% fixed carbon, indicating that it is very rich in the available carbon needed for the carbothermal reduction reaction. It also contain negligible ash content. These results give the amount of the kaolinite ($2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$) present in the beneficiated clay (91.7 wt%) and the amount of fixed carbon in the coal (85.9 wt%)

which served as the basis for computing the proportions of kankara clay and onyeama coal in the mixture needed for the carbothermal reduction. The mix calculations are as presented in Appendix A . The calculations were based on the theoretical reaction equation between kaolinite and carbon in the presence of nitrogen (equation 2.1). The amounts therefore needed according to the equation is approximately 80 wt% kankara clay and 20 wt% onyeama coal, a mix ratio of 4:1.

The thermal treatment of the clay - coal mixture in nitrogen atmosphere as carried out using the locally manufactured furnace and locally fabricated reaction chamber (saggar), was monitored by a Chromel thermocouple connected to a chart recorder. Table 4 and 5 present the calibration results for the two thermocouple used.

Calibration was carried out using Heraeus furnace (electrically fired) under the following operating conditions:

Chart speed - 2 mm/min.
Max. e.m.f. - 50 mV
Room temp. - 28^{0}C

The temperature, the e.m.f, the distance and the time were obtained from the chart and reported as Table 4.

Table 4 Calibration Results For the Test and First Production Run

Temp. (^{0}C)	e.m.f. (mV)	Distance (mm)	Time (min.)
100	3.00	7.0	3.5
200	6.25	11.0	5.5
300	9.00	17.0	8.5
400	11.50	25.0	12.5
500	14.00	33.0	16.5
600	16.50	45.0	22.5
700	19.00	59.0	29.5
800	22.00	84.0	42.0
900	24.50	105.0	52.5
1000	28.00	124.0	62.0
1100	30.75	143.0	71.0
1200	32.50	208.0	104.0
1300	35.00	254.0	127.0

The second and third calibration was carried out using Heraeus furnace under the following condition:

Chart speed - 2 mm/min and 1 mm/min
Max. e.m.f. - 50 mV
Room temp. - 28^{0}C

The e.m.f. , the distance, the time and the temperature were obtained from the chart and reported as Table 5.

Table 5 Calibration Result for the Second and Third Production Runs

Temp. (^{0}C)	e.m.f. (mV)	Distance (mm)	Time (min.)
200	10.00	9.0	4.5
300	14.00	12.0	6.0
400	17.00	18.0	9.0
500	20.50	24.0	12.0
600	24.25	32.0	16.0
700	28.00	37.0	37.0
800	32.00	44.0	44.0
900	36.00	51.0	51.0
1000	40.00	63.0	63.0
1100	44.00	74.0	74.0
1200	47.00	85.0	85.0
1300	51.00	124.0	124.0

Calibration curves were thus obtained from the foregoing results. Figures 16 to 19 show the calibration curves as plotted from the

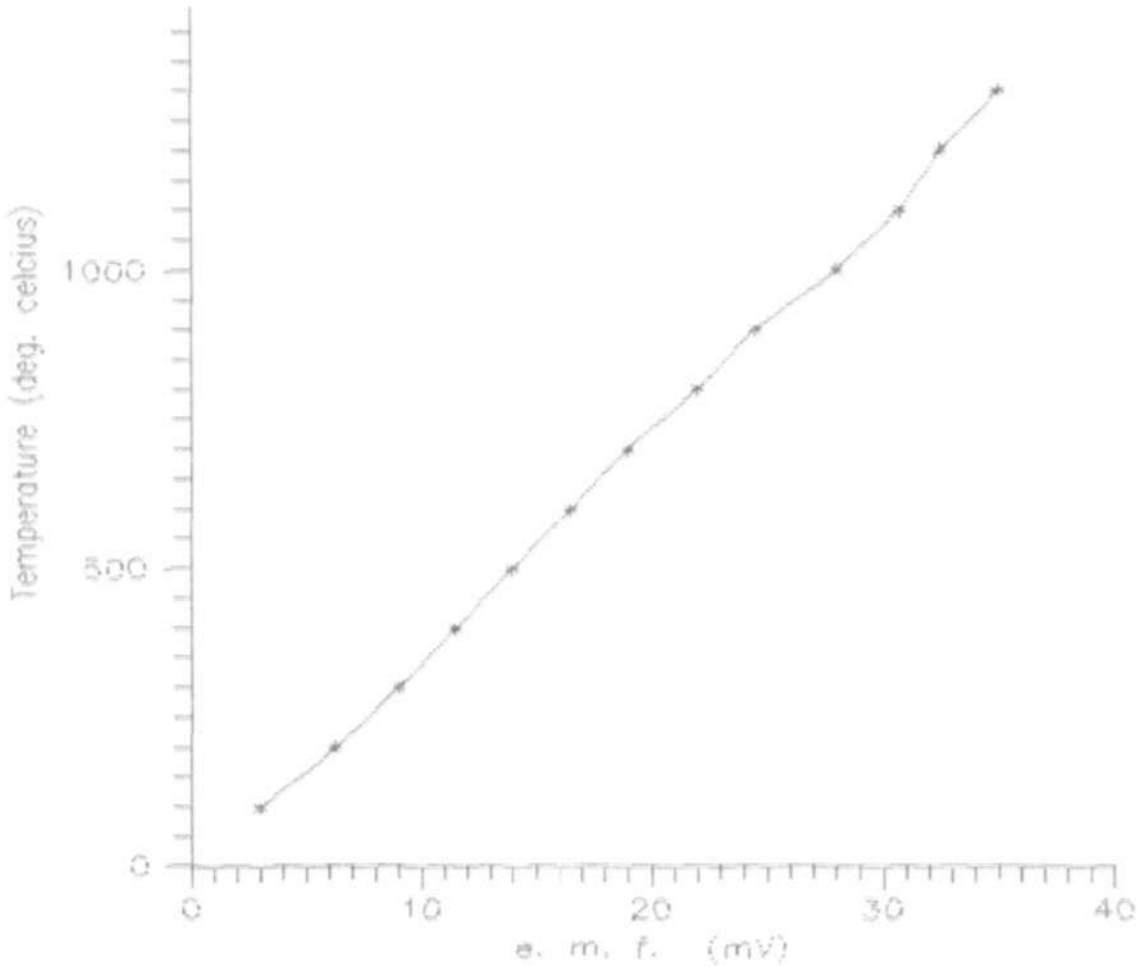


Figure 16 Temperature - e. m. f. calibration curve for the chart recorder and thermocouple used for the testing of the furnace and first production run

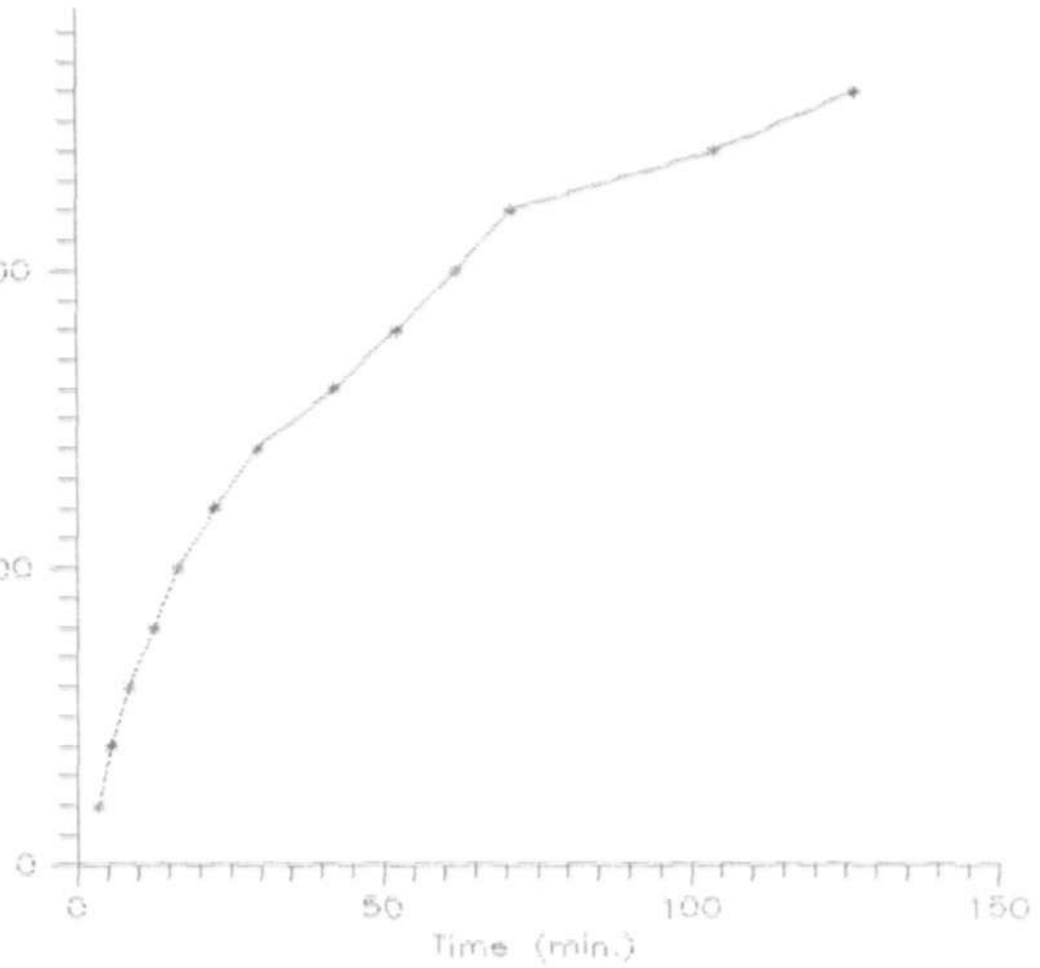


Figure 17 Temperature - Time calibration curve for the chart recorder and thermocouple used for the testing of the furnace and first production run

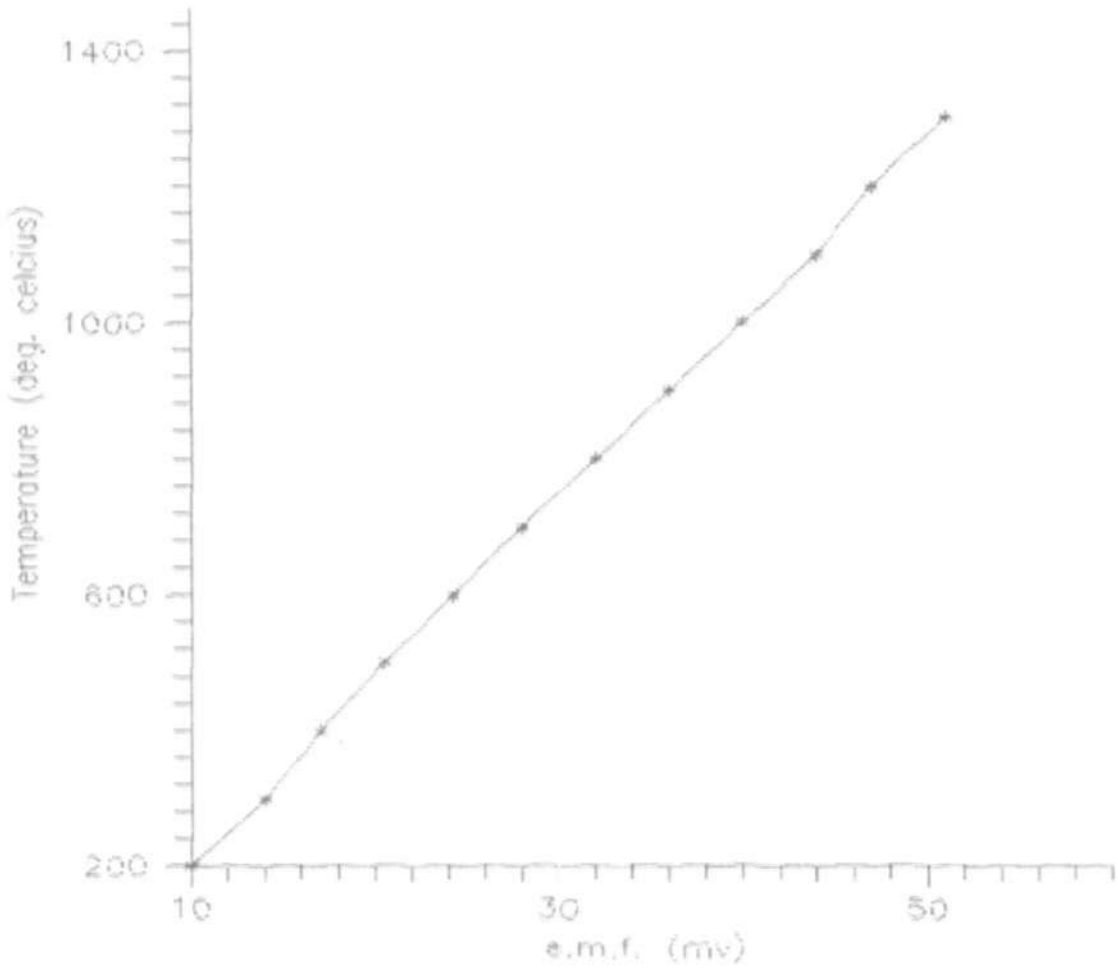


Figure 18 Temperature - e. m. f. calibration curve for the chart recorder and thermocouple used for the second and third production runs .

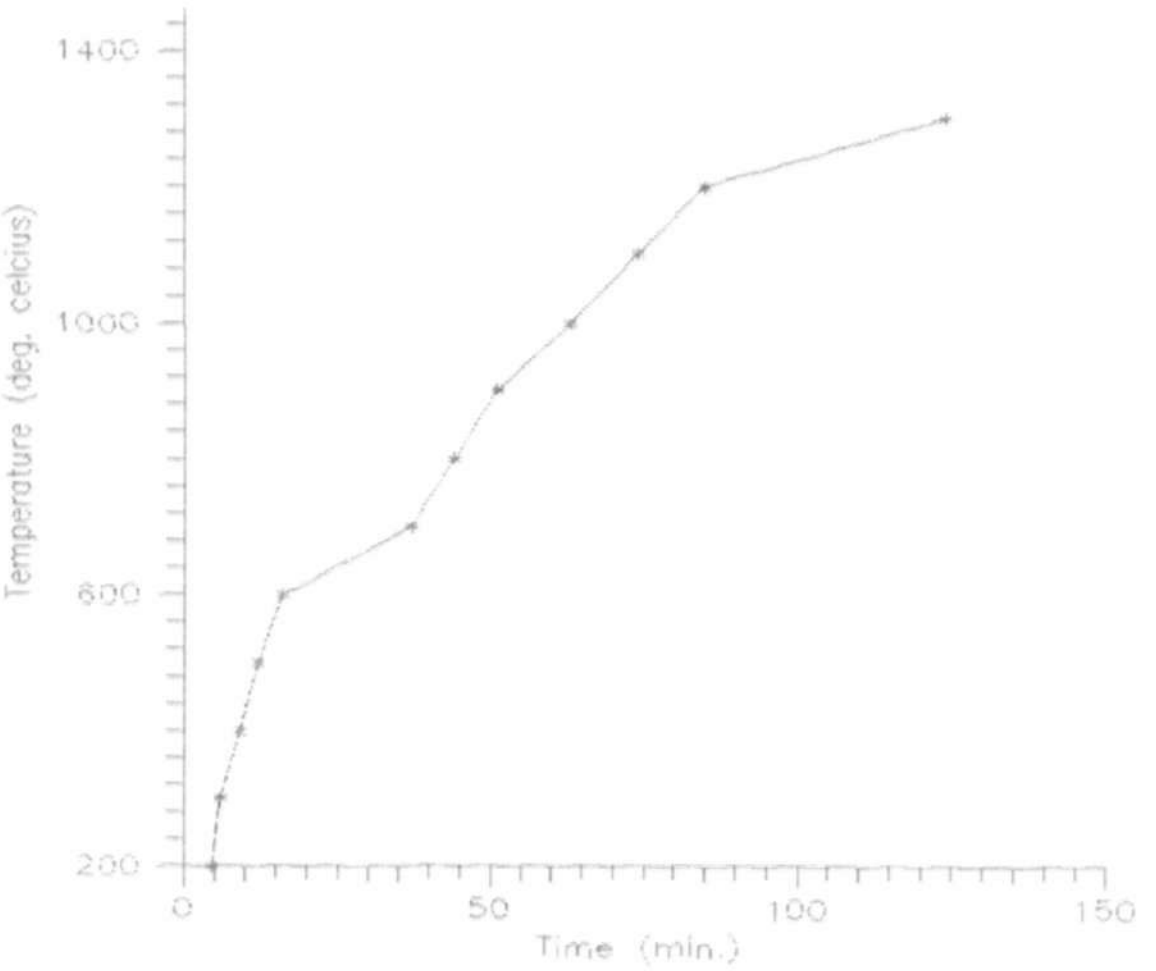


Figure 19 Temperature - Time calibration curve for the chart recorder and thermocouple used for the second and third production runs

The temperature progression for the testing of the furnace and the three production runs were extrapolated from the chart as compared to the calibration curves and the results are presented in Tables 6 to 9.

Table 6 Temperature Variation during the Testing of the Furnace

Temperature (^{0}C)	Time (hr)
730	0.24
785	0.59
820	0.80
860	1.59
920	3.07
970	4.20
1020	5.49
1060	7.07

Table 7 Temperature Variation for the First Production Run

Time (hr)	Temp. (°C)
0.37	800
1.45	840
2.87	880
3.53	880
4.03	920
4.82	990
4.98	1075
5.22	1175
5.87	1200
6.45	1260
7.00	1280
7.52	1300
8.07	1320
8.68	1340
8.78	1360
9.23	1360
9.67	1300
11.02	1300
11.28	1320
11.40	1340
12.90	1360
13.03	1320
13.23	1220

Table 8 Temperature Variation for the Second Production Run

Time (hr)	Temp. (°C)
0.03	435
0.17	580
0.38	820
0.50	885
0.66	945
1.02	1035
1.50	1115
2.00	1165
2.50	1200
2.90	1210
3.98	1250
4.17	1260
5.00	1260

Table 9 Temperature Variation for the Third Production Run

Time (hr)	Temp. (°C)
0.05	200
0.07	335
0.17	485
0.33	620
0.50	750
0.83	875
1.17	1000
1.50	1100
1.83	1165
2.12	1190
2.37	1200
2.50	1210
2.67	1225
2.98	1250
3.33	1275
3.75	1315

The firing curves for the testing of the furnace and the three production runs are as presented in Figures 20 to 23

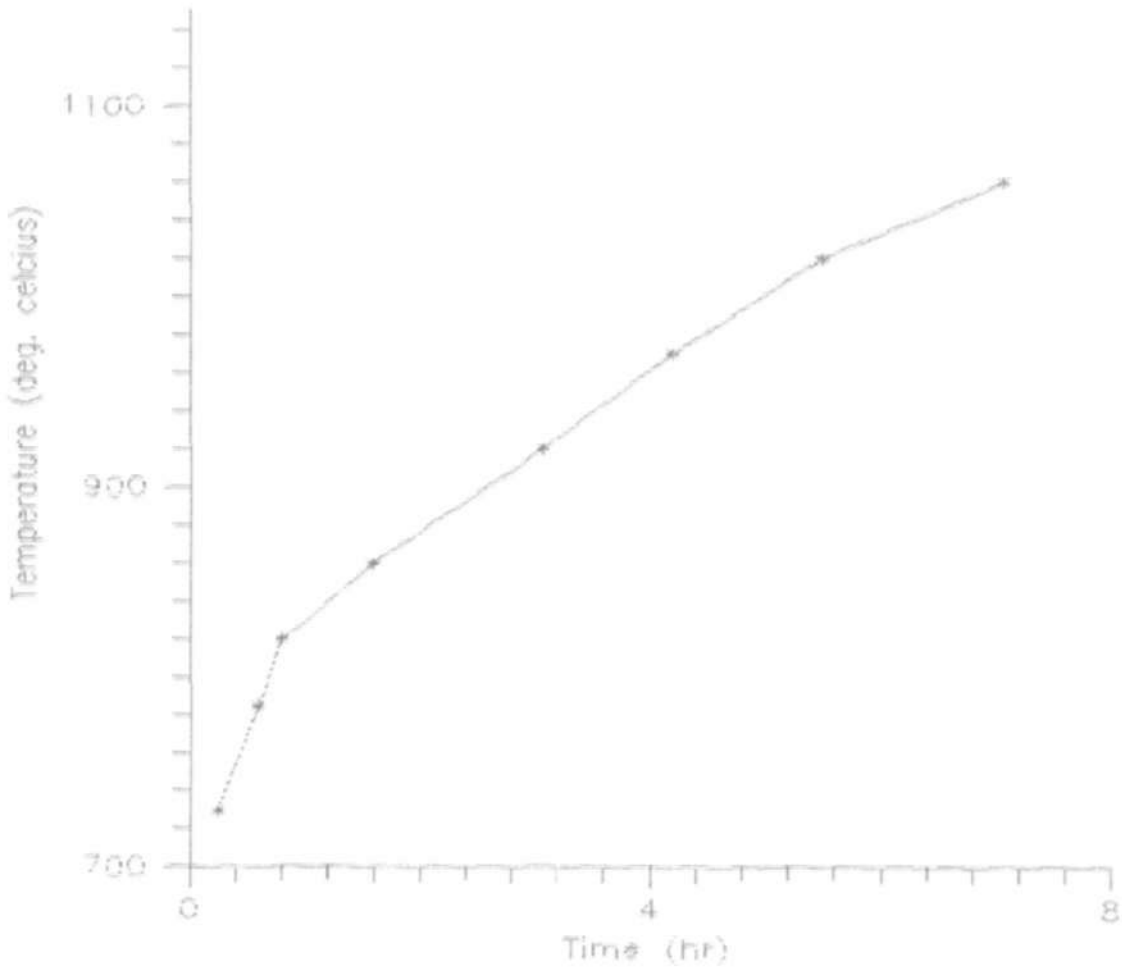


Figure 20 Firing Profile during the testing of the Furnace

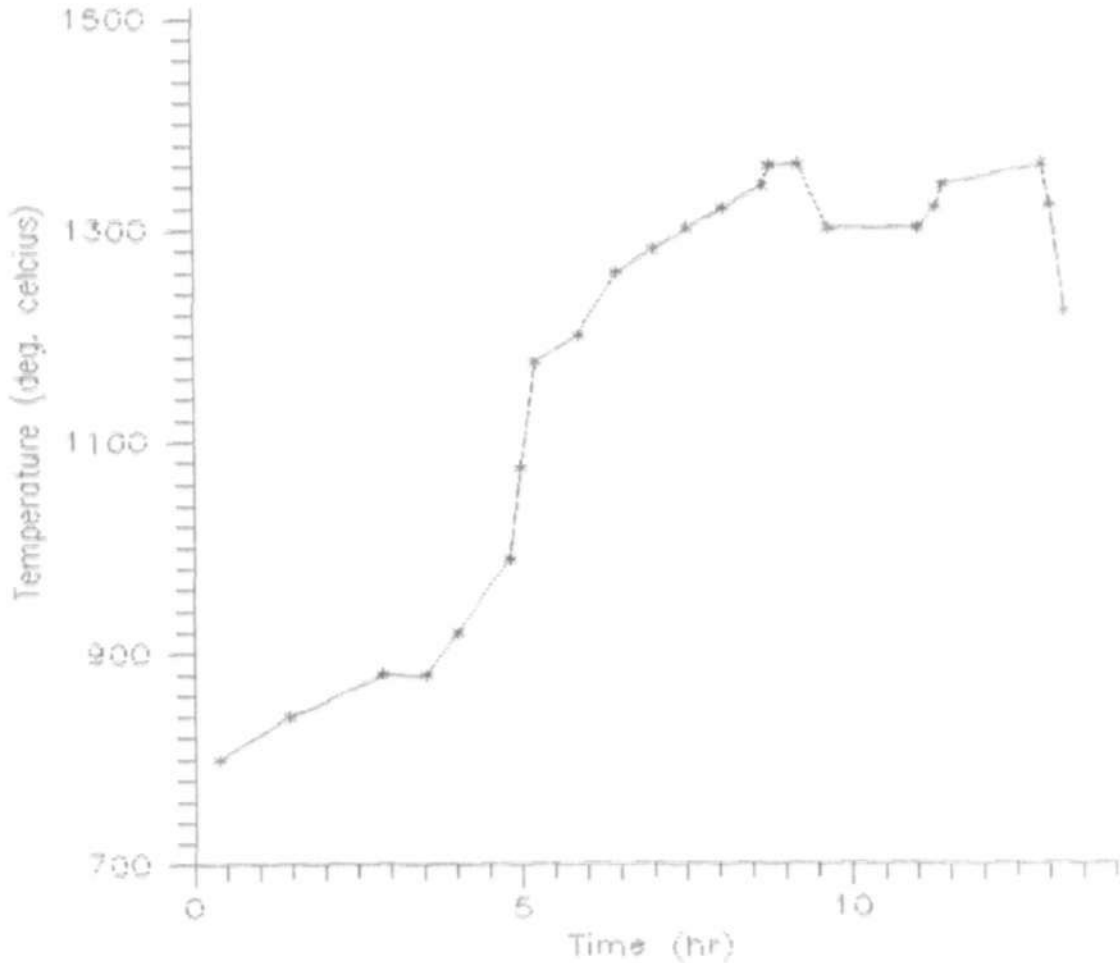


Figure 21 Firing Profile during the first production run

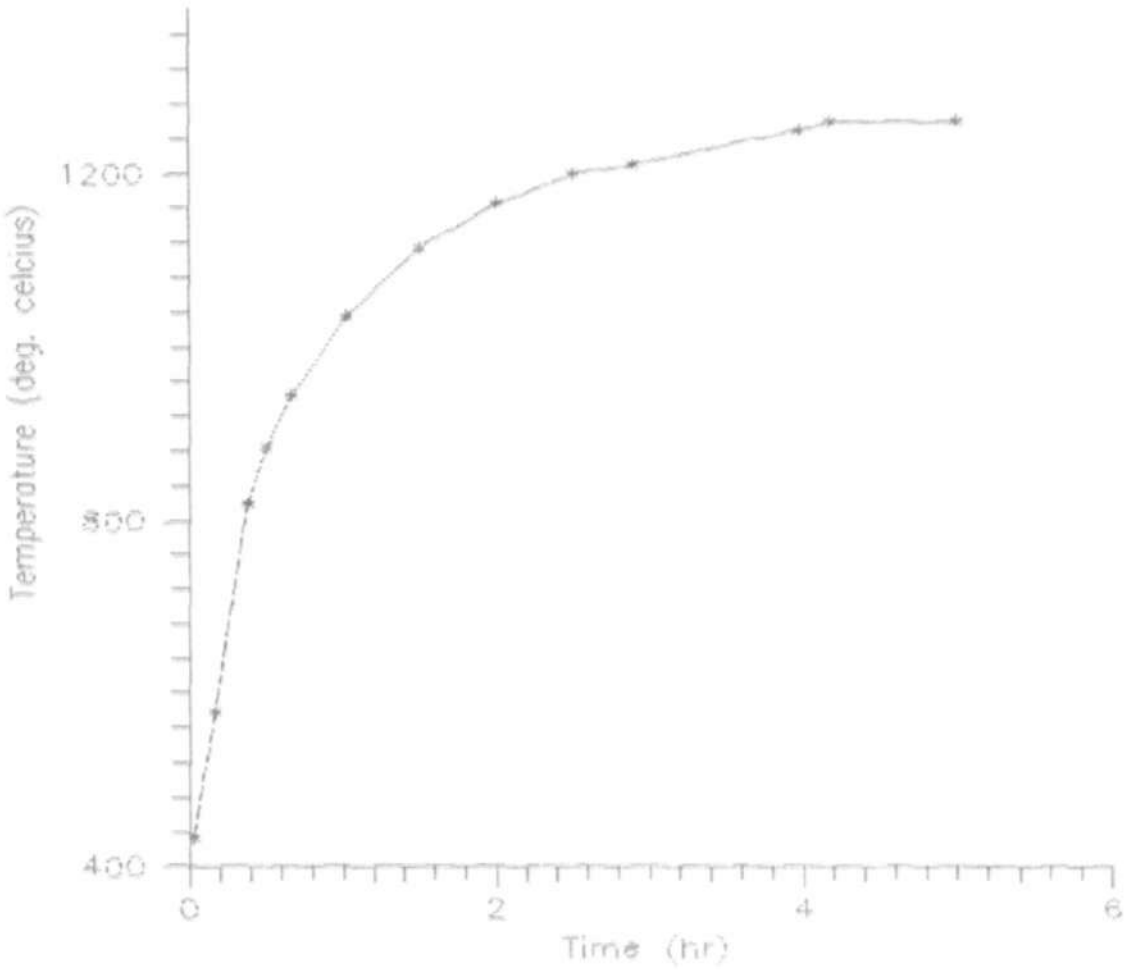


Figure 22 Firing Profile during the second production run

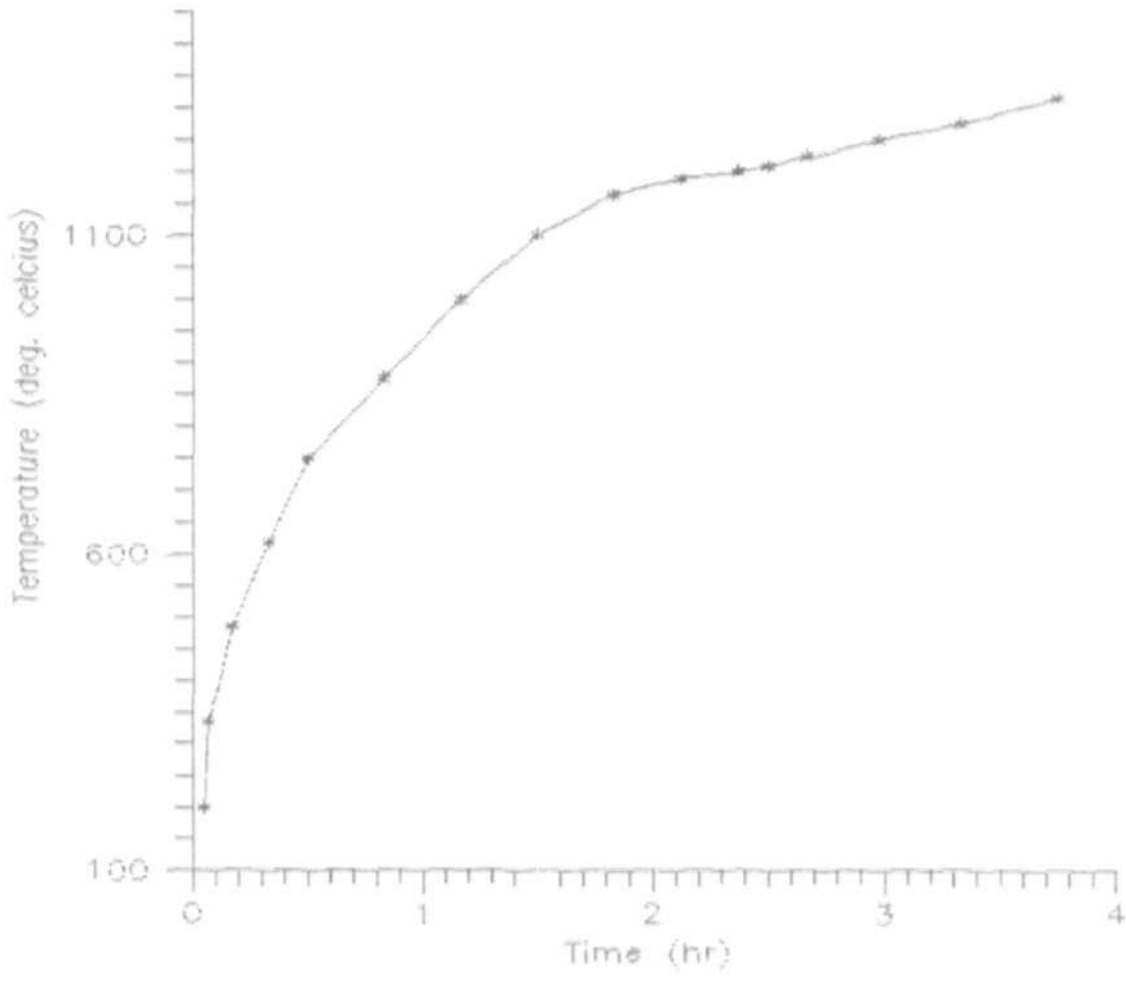


Figure 23 Firing Profile during the third production run

It can be seen from the Firing curves that the highest temperature of 1360^{0}C was attained during the first production run. The behavior of kaolinite on heating is well documented[1,2]. At about 500^{0}C, dehydration occurs giving an amorphous material (meta - kaolin) and at 1200^{0}C nucleation of mullite occurs. At the reaction temperature according to Higgins and Hendry, 1400^{0}C, the kaolinite is therefore already broken down into a mixture of mullite and free silica,

$$3(2SiO_2 \cdot Al_2O_3 \cdot 2H_2O) \longrightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2 + 6H_2O$$

(kaolinite) (mullite) (free silica)

And the isothermal formation of β-sialon after one hour at 1400^{0}C starts. In the present investigation, the highest temperature reached was 1360^{0}c for the first batch, for a limited period of time. This was partly because the furnace is a gas-fired one and a blower had to be incorporated tc enhance the fuel combustion, and also because the peak temperature could not be maintained for much longer.

This may have greatly affected the production rate as the furnace could not reach the required temperature of 1400^{0}c and the peak temperature could not be maintained for a sufficiently long period. A maximum soaking time of 4 hours at 1360^{0}C was achieved for the first run as compared to the 8 hours that was typical in literature. This indicates that the formation of β-sialon at the end of the short firing period may end up to be quite small.

Another indication of the extent of reaction is from the carbon monoxide concentration in the exhaust gases from the reaction chamber. The results of the Orsat analysis of the exit gas stream from the reaction chamber is as presented in Appendix B, whereas Figures 24 to 26 show the variations in concentration of the carbon monoxide and other associated gases from the reaction chamber with firing time.

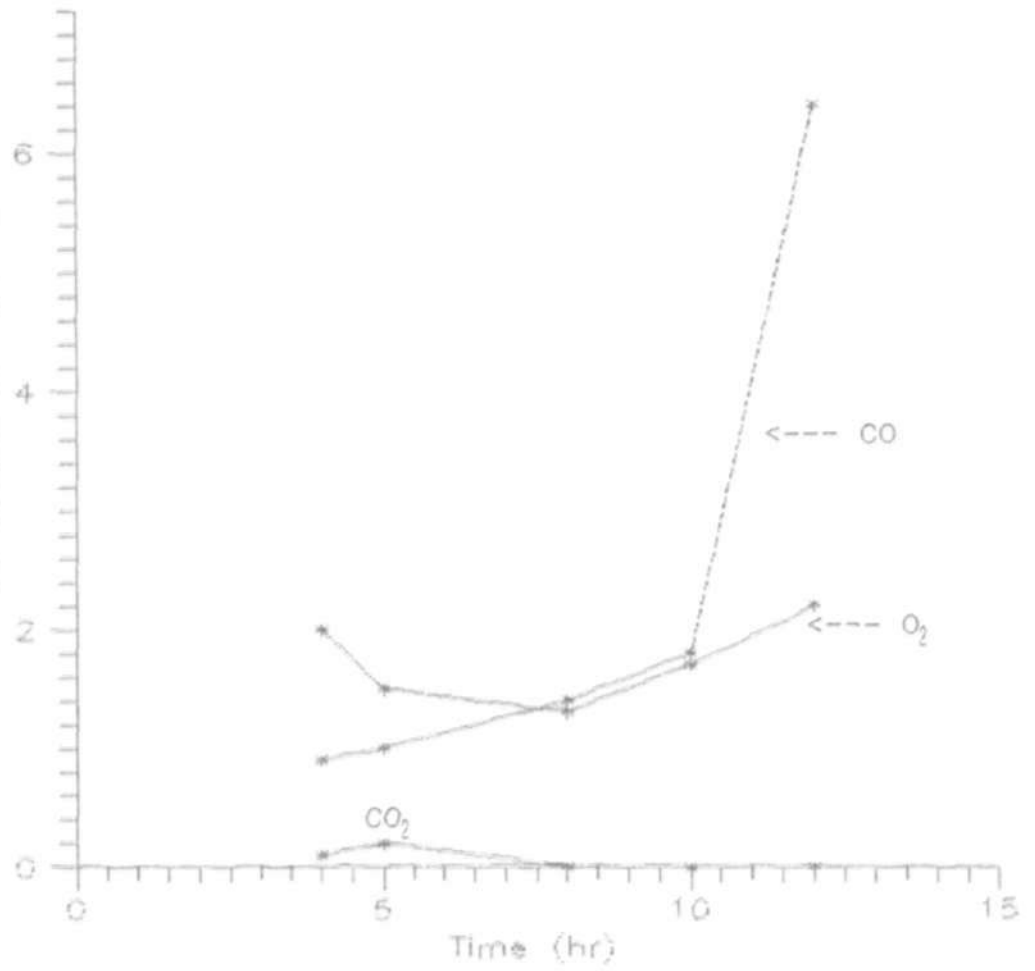


Figure 24 Gas composition in the exit gas stream from the saggar (first Production run)

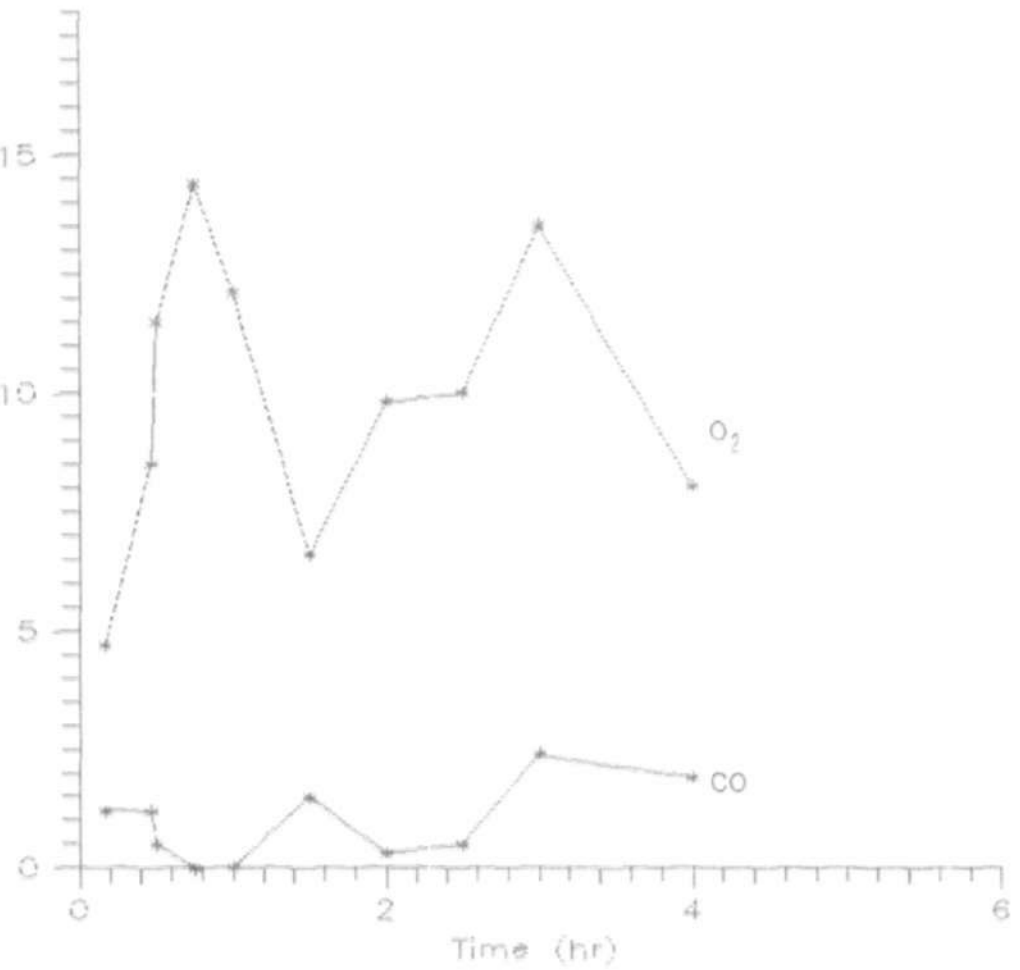


Figure 25 Gas composition in the exit gas stream from the saggar (second Production run)

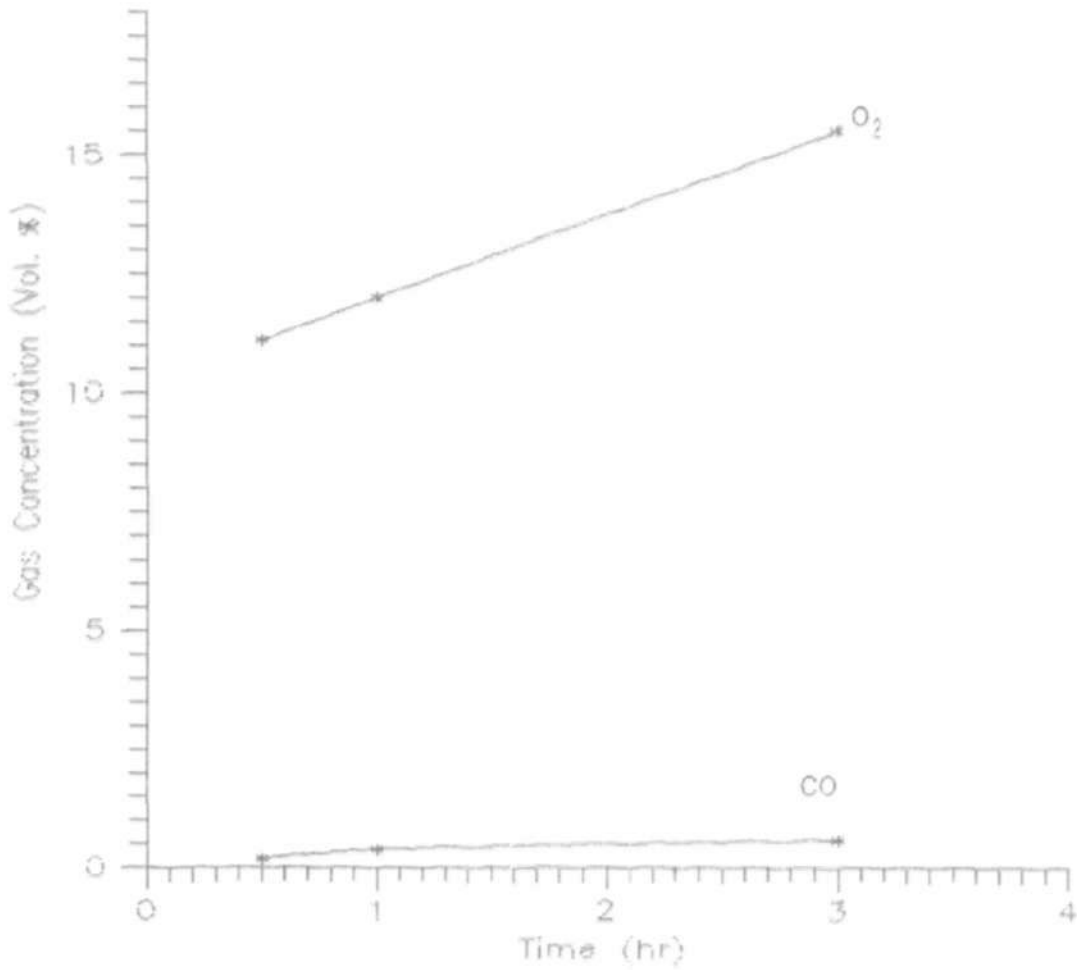


Figure 26 Gas composition in the exit gas stream from the saggar (third Production run)

According to the reaction equation (see Eqn. 2.1), carbon monoxide concentration increases as the reaction progresses but gradually decays as the carbon is removed from the sample by reaction with clay. Therefore monitoring the concentration of carbon monoxide in the exit gas stream can be an indicator to the extent of reaction taking place within the reaction chamber. Figures 24 and 25 has clearly shown that, the concentration of carbon monoxide increases with firing time implying that carbon is yet to be exhausted from the reaction chamber by reaction with clay and thus indicated that sialon material had just started to form.

Further to confirm whether or not sialon material has actually been formed, an x-ray diffraction analysis of the product formed to ascertain the crystalline phases present was supposed to have been carried out but due to lack of functional x-ray facilities, bulk nitrogen analysis of the products was carried out using Kjeldahl distillation apparatus and subsequent titration to obtain the amount of nitrogen present in the samples. However, rational analysis could have been a better alternative to nitrogen anaysis, but due to insufficient data (only three production runs) points necessary for rational analysis, bulk nitrogen analysis of the products was therefore carried out. This procedure, though wrong would give an estimate of the extent of nitridation achieved during the production runs. Table 10 gives the summary of results as obtained using the Kjeldahl method.

Table 10 Summary of Nitrogen Analysis

Parameter	Sample 1	Sample 2	Sample 3
Peak Temp.(°C)	1360	1260	1315
N_2 Flow rate (ml/s)	72.3937	143.6751	102.2325
Nitrogen, Kjeldahl method (g)	0.0147	0.0162	0.0160
% nitrogen	0.735	0.82	0.80
% β - sialon	2.97	3.32	3.23

From Table 10 it can be seen that the amount of nitrogen in the samples is very small indicating that sialon has not been substantially formed and that nitridation only occurred on the surface.

The amount of nitrogen in the theoretical formula of β-sialon of characteristic Z - value of 3 is about 25% indicating that every 100g of β-sialon formed is associated with 25g of nitrogen. But according to the results obtained (Table 10), the products formed contain just about 3% β-sialon, assuming that all the nitrogen estimated by the Kjeldahl method comes from β-sialon ($Si^3Al_3O_3N_5$) only.

This may be due to the fact that the peak temperature attained during firing was below the reaction temperature of 1400°C and was difficult to maintain for a sufficiently long durations. The production of β-sialon was reported to occur isothermally at 1400°C for upwards of 4 - 8 hours[1,2].

It can be seen from Figure 26 that oxygen concentration was increasing despite the fact that, the reaction is a reduction reaction in which oxygen in the kaolinite is partially reduced by carbon to carbon monoxide. The nitrogen gas used may have contained some unwanted concentration of oxygen. The suppliers of the nitrogen gas could not give specific impurity content of the gas and it could not be analysed. Any oxygen present in the nitrogen gas stream will naturally, on heating reacts with the carbon to produce carbon dioxide. Figures 24 to 26 clearly showed this trend and the production of β-sialon may have been suppressed by the presence of oxygen in the nitrogen gas stream and thus nitridation occurred only on the surface.

Another factor that could probably lead to low sialon formation is if the reaction chamber(saggar) had microcracks which may have allowed air into the high temperature reaction. This could cause channelling and would prevent the nitrogen from reaching the reaction zone.

The nitrogen flow rate is known to affect the formation of sialon; the higher the flow rate of nitrogen the more the sialon is formed. This can be seen from Table 10, that the highest amount of β-sialon formed is associated with the highest flow rate of the nitrogen gas.

It can also be seen that the peak temperature 1260 ^{0}C was obtained during the second production run and yet the amount of β-sialon formed was higher than the amount obtained for the first production run with peak temperature of 1360^{0}C. This has confirmed that actually the formation of β-sialon starts as from 1200^{0}C, immediately the nucleation of mullite starts[1,2]. However, substantial amount of β-sialon can only be realised at 1400^{0}C for some hours.

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

On the basis of the results of the investigations carried out, the following conclusions may be made.

1. A β-sialon production facility from locally available raw materials has been set up.

2. A reaction chamber (saggar) has been successfully fabricated from locally available raw materials using investment casting technique.

3. Small concentrations of β - sialon was obtained using the production facility (3% of the total product obtained) under the operating conditions achieved, which may be due to the relatively low temperature (1360°C) attained.

6.1 RECOMMENDATIONS

The following recommendations may be of assistance to future workers on the production of β-sialon from locally available raw materials; kankara kaolinite or any other local kaolinite, Onyeama coal or any other local coal.

1. An X-ray diffraction analysis of the sialon product should be carried out so as to ascertain the proportion of crystalline phases present whenever the facilities are functional.

2. Other local kaolinitic clays and local coals should be tried in the production of β-sialon.

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APPENDICES

APPENDIX A

CALCULATIONS OF MIX PROPORTIONS OF CLAY - COAL MIXTURE.

The reaction to produce β-sialon from kaolinite, carbon and nitrogen can be represented by the theoretical equation;

$$3(2SiO_2 \cdot Al_2O_3 \cdot 2H_2O)_{(s)} + 15C_{(s)} + 5N_{2(g)} = 2Si_3Al_3O_3N_5{}_{(s)} + 15CO_{(g)} + 6H_2O_{(g)}$$

From the stoichiometric equation, 3 moles of kaolinite will react with 15 moles of carbon and 5 moles of nitrogen at 1400°c to produce 2 moles of β - sialon ($Si_3Al_3O_3N_5$), 15 moles of carbon monoxide and 6 moles of water. Table A1 and A2 present the Chemical and mineralogical compositions of Kankara clay as determined by Ahmed (1986)[7].

Table A1 Chemical Analysis of Kankara Clay

Parameters	Raw Clay wt%	Beneficiated Clay (-200 mesh) wt%
L.O.I	14.00	13.91
SiO_2	47.23	49.47
Al_2O_3	38.54	36.08
Fe_2O_3	N.D	N.D
Total	99.77	99.46

N.D means not detected

Source: Ahmed (1986)[7]

Table A2 Mineralogical Composition of Kankara Clay

Mineral	Raw Clay wt%	Beneficiated Clay (-200 mesh) wt%
Kaolinite	83.4	91.7
Montmorillonite	n.d	n.d
Quartz	n.d	n.d
Mica	n.d	n.d

n.d means not determined
source: Ahmed(1986)[7]

According to Ahmed (1986)[7], kankara clay contains 83.4 wt% kaolinite on raw basis and when beneficiated through -200 mesh, the composition rises to 91.7 wt% kaolinite. In this study, kankara clay is to be used as beneficiated and therefore 91.7 wt% kaolinite would serve as the basis for computations of the mix proportions.

Onyeama coal is to be used as the source of the carbon required for the reduction reaction. According to the proximate analysis carried out, Onyeama coal contains 85.9 wt% fixed carbon. Table A3 gives the weights of the various components involved in the production of β-sialon according to the stoichiometric equation.

Table A3 Stoichiometric Amounts of Reactants and Products

Component	No. of moles	Mol. wt. g/gmol	Weight g
Kaolinite	3	258	774
Carbon	15	12	180
Nitrogen	5	28	140
β -sialon	2	283	566
Carbon monoxide	15	28	420
Water	6	18	10

Beneficiated kankara clay has a kaolinite content of 91.7 wt% and according to the stoichiometry, 774g of kaolinite will be needed for the reaction to complete. Therefore the weight of kankara clay needed is 774/0.917 = 844.0567g .

The Onyeama coal has a fixed carbon content of 85.9 wt% and according to the stoichiometry, 180g of carbon will be needed for the reaction to complete. Therefore, the weight of Onyeama coal needed to supply the carbon necessary for complete reduction reaction is 180/0.859 = 209.546g.

The clay - coal ratio is then given by;

844.0567/209.546 = 4.02 ~ 4

This implies that for every 4 parts of kankara clay 1 part of onyeama coal by weight would be required.

Fraction of kankara clay = 0.8 or 80%
Fraction of onyeama coal = 0.2 or 20%

APPENDIX B

RESULTS OF THE EXIT GAS STREAM ANALYSIS

Table B1 Orsat - Analysis Results for the First Production Run

Time (hours)	Carbon monoxide Vol.%	Carbon dioxide Vol. %	Oxygen Vol. %
4	0.9	0.1	2.0
5	1.0	0.2	1.5
8	1.4	0.0	1.3
10	1.8	0.0	1.7
12	6.4	0.0	2.2

Table B2 Orsat - Analysis Results for the Second Production Run

Time (hours)	Carbon monoxide Vol.%	Carbon dioxide Vol. %	Oxygen Vol. %
0.17	1.2	0	4.7
0.47	1.2	0	8.5
0.50	0.5	0	11.5
0.75	0.0	0	14.4
1.00	0.0	0	12.1
1.50	1.5	0	6.6
2.00	0.3	0	9.8
2.50	0.5	0	10.0
3.00	2.4	0	13.5
4.00	1.9	0	8.0

Table B3 Orsat - Analysis results for the Third Production Run

Time (hours)	Carbon monoxide Vol.%	Carbon dioxide Vol. %	Oxygen Vol. %
0.5	0	0.2	11.1
1.0	0	0.4	12.0
3.0	0	0.6	15.5

APPENDIX C

BULK NITROGEN ANALYSIS OF THE SIALON PRODUCTS OBTAINED

Table C1 gives the readings obtained from titration

Table C1 Readings From titration

Burette Readings	Sample 1	Sample 2	Sample 3	Blank
Initial (ml)	0.00	10.00	0.00	8.00
Final (ml)	9.50	18.30	8.60	18.00
Titre (ml)	9.50	8.30	8.60	10.00

CALCULATIONS

Weight of Products taken for nitrogen analysis = 2g
V_1 = vol. of 0.1N H_2SO_4 taken (blank value) = 20 ml
V_2 = vol. of 0.1N NaOH (titre value) used to neutralise the excess of the 0.1N H_2SO_4

The neutralisation reaction between the base and the acid can be represented by the following equation;

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

volume of base (NaOH) = Vb = 10 ml (Blank Value)
No. of moles (NaOH) = nb = 2
Concentration (NaOH) = Nb = 0.1N
volume of acid (H_2SO_4) = Va
No. of moles " = na = 1
Concentration " = Na = 0.1N

Therefore, $Na * Va * na = Nb * Vb * nb$

From the above equation the volume of the acid can be calculated as;

$$Va = Nb * Vb * nb/(Na * na)$$
$$= 0.1 * 10 * 2/(0.1 * 1)$$
$$= 20 \text{ ml (blank value)} = V_1$$

It can be seen that the volume of acid taken equals 20 ml
Weight of nitrogen in the sample can be calculated as;

$$(V_1 - V_2) (0.0014) \text{ g}$$

where, V_1 = Vol. of acid taken = 20 ml
V_2 = Vol. of base (0.1N NaOH)

For sample 1 V_2 = 9.50 ml

Therefore the amount of nitrogen in the sample is,

$$(20 - 9.5)*0.0014 = 10.5*0.0014 = 0.0147 \text{ g}$$

% Nitrogen in sample is,

$$0.0147*100/2 = 0.735$$

For sample 2 V_2 = 8.3 ml

The amount of nitrogen in the sample is,

$$(20 - 8.3)*0.0014 = 11.7*0.0014 = 0.0164 \text{ g}$$

% Nitrogen in sample is,

$$0.0164*100/2 = 0.820$$

For sample 3 V_2 = 8.6 ml

The amount of nitrogen in the sample is,

(20 - 8.6)*0.0014 = 11.4*0.0014 = 0.0160 g

% Nitrogen in sample is,

0.0160*100/2 = 0.80

The molecular weight of β -sialon is 283 g/g-mol
The 283 g per mol is associated with 70 g of nitrogen or 70/283 =0.2473 fraction of nitrogen in β-sialon.

Therefore, the amount of β-sialon in sample 1 is given as;

0.735/0.2473 = 2.97%

The amount of β-sialon in sample 2 is given as;

0.82/0.2473 = 3.32%

The amount of β-sialon in sample 3 is given as;

0.80/0.2473 = 3.23%

Table C2 summarises the results of the bulk nitrogen analysis as carried out using the Kjeldahl method.

Table C2 Summary of Results on Bulk Nitrogen Analysis

Parameter	Sample 1	Sample 2	Sample 3
Nitrogen, by Kjeldahl method (g)	0.0147	0.0162	0.0160
% nitrogen	0.735	0.82	0.80
% β - sialon	2.97	3.32	3.23