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by

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PRODUCTION AND CHARACTERIZATION OF SILICA REFRACTORY FROM RICE HUSK

by

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A Thesis

Submitted to the Postgraduate Studies Programme

as a Requirement for the Degree of

DOCTOR OF PHILOSOPHY

MECHANICAL ENGINEERING

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR,

PERAK

MAY 2013

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DEDICATION

This thesis is lovingly dedicated to my daughter, Jubilee Glorious Odufa Ugheoke-ben and my father, Mr. P.I.K. Ugheoke.

ACKNOWLEDGEMENTS

My greatest gratitude goes to GOD ALMIGHTY, whose mercies, grace and favour through JESUS CHRIST saw me through this programme.

I appreciate my Supervisor, AP. Dr. Othman Mamat whose meticulous, but constructive criticisms saw to the achievement of the high quality of this research. While keeping an eye on me, he gave me freehand to try out those thoughts. My Co-Supervisor, AP Dr. Bambang Ari-Wahjoedi would always keep his eagle eyes on those undotted “i’s” and uncrossed “t’s”. To both of them I would say I am eternally grateful.

Without the understanding and overwhelming support of my family- My wife Olere Ugheoke-ben and my sons: Lifted and Achiever, coming to study in UTP would have been impossible. The birth of my daughter- Jubilee during the programme was an accelerator. I thank you all for your love and support.

I thank University of Abuja and the Tertiary Education Trust Fund for the study Fellowship opportunity granted to me.

The Management of the UTP, through the Centre for Graduate Studies enlisted me on the Graduate Assistantship Scheme. This kind gesture is gratefully appreciated.

My appreciation goes to the entire staff of the department, especially Mr Mahfuzrazi B Misbahulmunir and Mr Jani B Alang Ahmad, the Technologists who assisted me in handling most of the equipment used in the course of this research.

My colleagues and friends- Madam Adibah Amir, Mebrahitom Asmelash and several others too numerous to mention, were quite inspiring. I say thank you all.

Above all, I want to thank Pastors Watson and Christina and all CGBC Ethnoi members for their prayers and warm fellowship.

ABSTRACT

Rice husk was thought to be a renewable source of good silica, which can help prevent cracking of silica refractories in the temperature range 100-600°C. The work reported in this thesis aimed to develop and optimize a fast process for high purity silica production from rice husk, as well as apply the silica produced from the process to carry out optimized laboratory scale manufacture of hot-face, stand-alone silica refractory. Thus, a hydro thermo-baric (HTB) process was developed to aid the fast production of rice husk silica (RHS). The parameters of the HTB process were optimized using full factorial design of experiments. The RHS obtained from the HTB process was characterized in terms of particle size, pore volume, surface area, structure and morphology. Also, the parameters that affect the production of RHS refractory using PEG8000 as binder and $Ca(OH)_2$ as dopant (mineralizer) were investigated and their optimal values obtained using the one-variable-at-a-time (OVAT) method.

The results of the characterization procedures of the HTB processed RHS showed the product to be amorphous, with high BET surface area (about $133m^2/g$) and porosity (pore volume- $0.2813cm^3/g$), having particle average size of 117nm. The parameters (firing temperature, green compaction pressure and quantity of mineralizer) that affect the production of rice husk silica refractory were investigated. The optimal value of the dopant ($Ca(OH)_2$) was determined to be around 1.4%. The research investigations showed that an optimum pre-firing temperature should be chosen from the range 1250 to 1350°C, since the highest modulus of rupture (MOR) necessary for handling the produced refractories occurs within this range, and was consequent upon the tridymitization of the refractory body within this temperature range. The compaction pressure range that is optimal for good fired density, apparent porosity and MOR falls between 90 and 110MPa. The thermal expansion behavior study of RHS refractory monitored between 25 to 1500°C showed sudden expansion of 0.7% occurring at 220°C and was due to the transformation of α- to β- cristobalite. The highest expansion reached (0.85%) occurred within the temperature range of 650 to 850°C, remained almost constant for the investigated temperature range. It was not high enough to cause macro cracks in the refractory. MOR, apparent porosity, bulk density, refractoriness and reheat change are reported and they all met applicable standards.

ABSTRAK

Sekam padi telah berfikir untuk menjadi sumber yang boleh diperbaharui yang baik silika, yang boleh membantu mencegah masalah keretakan silika refraktori dalam julat suhu 100-600°C. Kajian yang dilaporkan dalam tesis ini bertujuan untuk membangun dan mengoptimumkan proses yang pantas untuk menghasilkan silika daripada sekam padi pada sekala makmal yang optimum bagi pembuatan permukaan panas, dan refraktori antara-muka-terma tunggal. Maka, satu proses yang dikenali sebagai hidro termo-baric (HTB) telah dibangunkan untuk meningkatkan kadar pengeluaran nanosilika daripada sekam padi. Parameter HTB proses akan dioptimumkan melalui eksperimen. Silika sekam padi (RHS) yang diperolehi daripada proses HTB disusun maklumatnya kepada saiz zarah – zarah, isipadu liang, keluasan permuakaan, struktur dan bentuk. Parameter yang mempengaruhi penghasilan silika sekam padi refraktori dengan mengunakan PEG 8000 sebagai bahan pelekat dan kapur mati sebagai pendopan (mineralizer) telah dikaji dan nilai optimum kajian diperolehi menggunakan kaedah "one-variable-at-a-time" (OVAT).

Keputusan analisa pencirian ke atas (RHS) yang dihasilkan dengan proses HTB menunjukkan produk ini merupakan armofus dengan luas permukaan BET yang tinggi (kira-kira 133 m^2/g) dan keliangan (isipadu liang-0.2813cm^3/g) serta mempunyai purata saiz zarah 117 nm. Parameter-parameter (suhu pembakaran, tekanan pemadatan hijau, kuantiti mineral) yang mempengaruhi penghasilan silika sekam padi refraktori telah dikaji. Nilai optimum pendopan Ca(OH)2 telah ditentukan sekitar 1.4%. Kajian penyelidikan menunjukkan suhu pra-pembakaran yang optimum perlu dipilih adalah diantara 1250°C hingga 1350°C, bersesuaian dengan nilai modulus pepecahan (MOR) yang diperlukan untuk mengendali penghasilan refraktori berada dalam lingkungan suhu ini. Julat tekanan pemadatan yang optimum adalah perlu untuk memastikan ketumpatan pembakaran yang baik, keliangan nyata dan MOR berada pada lingkungan 90 dan 110 MPa. Sifat pengembangan haba RHS refraktori kajian yang diperhatikan dalam lingkungan 25°C – 1500°C menunjukkan pengembangan secara mendadak sebanyak 0.7% pada suhu

220°C disebabkan transformasi α- to β- kristobalite. Pengembangan paling tinggi (0.85%) berlaku diantara suhu 650°C – 850°C, hampir kekal untuk julat suhu yang dikaji, dan tidak cukup tinggi untuk menyebabkan pemecahan macro dalam refraktori berlaku. Modulus pepecahan, keliangan nyata, ketumpatan pukal, kerefraktorian dan perubahan pembakaran semula telah dilaporkan dan keputusan yang diperolehi telah mencapai standard kelayakan untuk digunakan dalam ketukar kok.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

ABBREVIATION	MEANING
AP	Apparent porosity
BD	Bulk density
BET	Brunauer–Emmett–Teller method
DRH	Dry rice husk
EDX	Electro-dispersive x-ray
HMOR	Hot modulus of rupture
HTB	Hydro thermo-baric
LS	Linear shrinkage
MOR	Modulus of rupture
OVAT	One-variable-at-a time
PCE	Pyrometric cone equivalent
PLC	Permanent linear change
RHS	Rice husk silica
RUL	Refractoriness under load
SOKT	Soaking time
TEMP	Temperature
WA	Water absorption
WHTR	Water to husk ratio

CHAPTER 1

INTRODUCTION

1.1 Chapter Overview

This chapter lays the foundation for the entire research undertaken. Section 1.2 gives the study background information, laying foundation for the work. This is followed by the research statement of problem in section 1.3, culminating in the formulation of research aim and objectives presented in section 1.4. The scope of the research is presented in section 1.5. The thesis structure is presented in section 1.6. The chapter closes with section 1.7 which presents the chapter summary.

1.2 Background of Study

High temperature operations are involved in almost all the industries dealing with the treatment of ores and other materials for the manufacture of metallurgical, chemical, and ceramic products. Equipment used in such high temperature operations are called furnaces. Furnaces are often lined with some materials of ceramic classification called refractory. A refractory material is one which can withstand high temperatures (usually greater than 538°C) [1] and resist the action of corrosive liquids and dust-laden currents of hot gases [2].

In general a classification term, silica refractory (or Dinas) is a refractory with silica (SiO_2) content of at least 93%. In the production of silica refractory, the traditional raw material used is quality rocks, which may exist in many allotropic forms, predominantly quartz. Various grades of silica bricks have found extensive use in the iron and steel melting furnaces, coke ovens and the glass industry. Among the good properties of silica refractory reported in the literature [3, 4] are high fusion point (up to 1730°C), high resistance to thermal shock (spalling) above 600°C and their high refractoriness under load. One peculiar characteristic of silica brick is that it does not begin to soften under high loads until its fusion point is approached and in fact as stated in Chesters [3], it can carry a load of about 1MPa within a few degrees of its melting point (1710-1730°C). Also, according to Kraplya *et al.* [4], this behavior contrasts with that of many other refractories, for example alumino-silicate materials, which begin to fuse and creep at temperatures much lower than their fusion points. Kraplya *et al.* [4] also mentioned other advantages of silica bricks to include flux and slag resistance and volume stability above 600°C. Apart from these, silica refractory has good thermal conductivity, such that it does not necessarily require the use of back-up insulation during furnace construction, which makes for furnace chamber optimization.

It has been observed [5] that silica refractory exhibits complex phase transformations due to the presence of a combination of low tridymite, α-cristobalite and residual α-quartz. If these three phases are present in significant quantities within the refractory body, they would result in after-expansion phenomenon. The magnitude of the after-expansion phenomenon could be so high as to result in crack formation at temperatures of between 117–163, 200–270 or 573°C, which correspond respectively to the inversions of low to high tridymite; α- to ß-cristobalite and α-quartz to ß-quartz. For this reason, silica refractory has been adjudged to have poor thermal shock resistance at low temperatures (below 600°C) [6]. Therefore, heating a furnace lined with silica refractory past this temperature range has to be gradual and pursuant to this effect, Gilchrist [7] suggested a heating rate of not more than 10°C rise per hour, if the shattering phenomenon in silica refractory bricks may be minimized. Consequently, longer periods are required to soak the furnace up to the working temperature, resulting in great energy demands and losses, as well as man-hour wastage.

One other problem of silica refractory development has to do with the progressive exhaustion of the non-renewable source (the earth) of the raw material used and it was therefore recommended [8] that research and development should move in the direction of alternative materials, if growth in the industry was to be sustained. This recommendation notwithstanding, current literature directly related to silica refractory research and development is quite sparse. Even the ones that were done [9-13], only helped in corroborating the findings of earlier research era. There were no major milestones reported. They have used the same style as the early researchers, only testing materials from different parts of the earth and have therefore, not come up with better ways of producing silica refractory, with superior performance. Specifically, the great challenge observed in silica refractory, that is, very poor spalling resistance between the temperatures of 100 and 600°C, is yet to be circumvented.

There is not a record to show how the optimal value of a mineralizer used in the manufacturing process could be determined. It is reported in [2, 3] that pressure is applied to the bricks after batching and mixing, but how much of this pressure is suitable for the right level of porosity, bulk density and thermal conductivity is not reported in any literature, at least in this era.

In terms of raw materials, only a few researchers [9, 10] reported the use of local sand for silica brick production and characterization. Yet, the centrality of raw materials in silica refractory research and development has been and will continue to be important to the refractory industry. This is because raw materials affect batching/ mixing, product quality, properties, innovation and advancement and profitability [14], giving credence to the call for research into renewable raw material sources [8].

However, current research [15-17] has shown that there could be an alternative, renewable source of silica: rice husk, rather than the earth. It is therefore, the author's hypothesis that it is possible to continue research in silica refractory development, in order to minimize the problems identified in the review of literature and make them more attractive than ever, tapping from the advances in science and technology, especially by leveraging on nanotechnology and the opportunity of the abundance of rice husk as an agro-waste in many African and Asian countries, including Malaysia.

1.3 Statement of Problem

It is already stated that silica refractories combine the advantages of high refractoriness and good thermal conductivity, thus making its use in furnace construction as a way of reducing cost of furnace fabrication and maintenance. However, silica refractory has the disadvantage of poor spalling characteristics when heating past the temperature range of between 100–300°C, 573 and 600°C and also, when cooling below 300–100°C. At these mentioned temperature ranges, the bricks shatter or crack, except extra caution is taken through very slow heating or cooling rate, which results in incurring expenses in energy and time (in terms of man-hour losses). The failure of these bricks in these mentioned temperature ranges is a direct consequence of the complex phase transformations that take place within the temperature ranges, resulting in varying volumetric dimensional changes. Opaline silica does not undergo these complex phase transformations, as some literature [5, 6] have shown, because of its structure (amorphous) and chemistry (being hydrated).

Apart from this observed drawback of poor spalling resistance at temperatures lower than 600°C, raw materials for the production of silica refractory have been from earth and earth related sources. Decades ago, Davies [8], in reviewing British sources of silica posited that for the production of high quality silica refractory bricks, noted the fast depletion of (progressive exhaustion, without renewal) silica refractory raw materials and therefore, recommended that research and development should move in the direction of alternative materials, if growth in the silica refractory industry was to be sustained. This recommendation was bolstered by the statement made by Semler [14], when he stated that raw materials have been (and will continue to be) important to the refractory industry because they affect batching/ mixing, product quality, properties, innovation and advancement and profitability. It was therefore, necessary to identify sources of renewable raw materials for the sustained production of and growth in the silica refractory industry.

Rice husk has been identified [15-17] as a renewable source rich in opal silica so it could be used as a raw material source of silica for refractory production. Obtaining high purity silica from rice husk has been a subject of research, with some authors [18, 19] using fluidized bed combustion method, while the sol-gel (or acid-base precipitation) method was used by Kalapathy *et al.* [20, 21] to produce silica of purity a little over 97%, with lower sodium content from rice husk ash. Liou [22] produced amorphous nano-structured silica powders with average particle size of 60 nm and high specific surface area using a combination of acid leaching, nonisothermal decomposition of rice husk in an air atmosphere at temperatures between 27 and 727°C using different heating rates, followed by basic treatments and water washing. Real *et al.* [23] and Yalcin and Sevinc [24], have demonstrated that homogeneous size distribution of nanometric silica particles could be obtained by burning acid pre-treated rice husk at 600–800°C in a pure oxygen atmosphere. The fluidized bed combustion method can only produce rice husk ash without any improvement in the purity level of the silica obtained. It is therefore not suitable for high purity rice husk silica production, which is needed in the refractory industry. The major methods that have been used to process high purity rice husk silica (RHS) are the acid leaching and the sol-gel processes, which involve the use of highly concentrated acids or bases. Reviewing these methods however, it is not difficult to observe some obvious problems. One of these problems is that the chemicals used in the processes are highly corrosive, with dangerous and environmentally unfriendly by-products. Laboratory use of these methods requires extra precautions and high investment and maintenance costs on HSE (health, safety and environment) equipment and procedures. This would translate to high cost and high risk levels if the sol-gel based processes are to be used for large-scale production of high purity silica, up to levels required in most industries. So, even though many authors [15-17] concluded that rice husk is an excellent source of high-grade amorphous silica, commercial production of high quality grade silica from rice husk is still in abeyance. This therefore, calls for research into more economic ways to mass produce high purity silica from rice husk to support supplies to the industries that use it as raw material.

From the foregoing, there is therefore need to develop a new process for the production of high purity silica from rice husk, optimize the production process as well as characterize the silica obtained from the process. The obtained high purity rice husk silica (RHS) would be used to manufacture RHS refractory. The questions that need to be answered include: what factors affect production of silica from rice husk and what are their optimum values? What are the optimum values of the factors that affect the production of RHS refractory? What are the magnitudes of the dilatometric changes that occur in silica refractory produced RHS and at what temperatures? What is the nature of the phase changes that occur alongside and at the temperatures at which these dilatometric changes are observed? What consequences, if any, do these dilatometric changes have on structural stability of the refractory? What is the refractoriness of rice husk silica refractory and what physical and mechanical properties do they exhibit at low temperatures? These are the questions this research sets out to answer.

1.4 Research Aim and Objectives

This research aimed to develop and optimize a fast process for the production of high purity silica from rice husk, as well as apply the silica produced from the process to carry out optimized laboratory scale manufacture of hot-face, stand-alone silica refractory.

To achieve this aim, the research targeted the following specific objectives:

i) Production of high purity silica from rice husk using a new process- the hydro thermo-baric (HTB) process. This entailed:

  - Identification of HTB process factors
  - Characterization of the produced silica
  - Optimization of the parameters of production using the full factorial design of experiment method;

ii) Production and characterization of samples of silica refractory from the silica obtained from objective (i) using polyethelyne glycol (PEG) as binder, leading to the determination of the optimum:

  - percentage of mineralizer ($Ca(OH)_2$)
  - firing temperature
  - compaction pressure;

iii) Investigation of the thermal response of the fired RHS refractories in terms of thermal:

  - thermal expansion characteristics

- pyrometric cone equivalent (PCE)
- reheat change and linear shrinkage
- morphology and mineralogy.

1.5 Scope of Research

In the production of RHS using the developed HTB process, chemical kinetics taking place inside the reactor did not form the focus of this research, rather, consideration and attention was given to the effects the process had on the product (RHS) purity (determined by XRF), structure (determined by XRD) and morphology (analyzed by FESEM and EDX). The temperature investigated in HTB process ranged between 264 and 300°C. The process parameters optimized are water to husk ratio, soaking time and temperature. The reactor used had a maximum capacity of 150ml.

In actual industrial practice, refractory characterization is divided into characteristic data properties, design related properties and performance/service related properties (see section 2.6). The focus of the characterization undertaken in this research relates to the characteristic data properties, which help in the design and manufacture of refractories. Although, the scope of the research covered the characterization of the physical properties (apparent porosity and bulk modulus) using the applicable ASTM standard (refer to chapter 3), thermal properties (thermal expansion behavior, linear shrinkage and permanent linear change) and mechanical properties (modulus of rupture (MOR)), the focus of the characterization of the refractory was on the thermal expansion behavior investigated by the use of dilatometer. This is because knowledge of the values of the dilatometric changes occurring in the refractory would help to determine whether cracking of the refractory would occur or not. Also, the RHS size range considered in this research is at the submicron (~117nm) level. However, performance or service related characterization of the refractory (such as creep in compression, refractoriness under load and hot modulus of resistance) is excluded from this study as experiments relating to such investigations require specialized equipment not available in Malaysia.

In the same vein, the definition of "production" both in the title of the research and in the work carried out refers to laboratory scale production, but with laid down parameters for industrial scalability.

1.6 Thesis Structure

The thesis is divided into five chapters. Chapter one established the reasons for undertaking the research. Chapter two is divided into four sections. Amongst these four sections, two of them are major sections: sections three and four. Section 2.3, which is a review titled "A brief Survey of the Literature on Silica Refractory Research and Development: a Case for Silica Obtained from Rice Husk" has already been published in Defect and Diffusion Forum. Section 2.4 presents a review titled "A critical Assessment and New Research Directions in Rice Husk Silica Processing Methods and Properties", which has also been published by an ISI journal.

Chapter three reports the methods used in realizing the specific objectives of the research. As stated in section 1.4, the specific objectives are three in all, so chapter four is divided according to these objectives. Section 4.2 titled "Production of Silica from Rice Husk: Process Development and Product Characteristics" deals with objective (i) of the research and has been published by Inderscience publishers in the International Journal of Materials Engineering Innovation. Section 4.3 is titled "RHS Refractory Production and Parameters Optimization" and treats objective (ii) of the research. It has also been published in the journal of the Australian Ceramic Society. Objective (iii) of the research has been presented in section 4.4, which is titled "Thermal Expansion Behavior, Phase transitions and some Physico-Mechanical Characteristics of Fired Doped RHS Refractory" and has been published by the Springer's Journal of Applied Ceramics. Chapter three is essentially a compilation of the methods used in these various articles. Chapter five presents concluding remarks and recommendations for future research.

1.7 Chapter Summary

In summary, the motivation, aim and objectives of this research have been vividly stated and these were pursued in the course of the research. The next chapter is dedicated to the review of literature, which informed the basis for establishing the aims of this research as stated in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Chapter Overview

This chapter begins with section 2.2, which reviews extant literature on refractory classification, in order to establish the place of silica refractory in the industry. This is followed by a review of the state of research and development in silica refractory presented in section 2.3, which led to the identification of the research gaps in the field. A case for new raw materials, that is, the use of rice husk silica in the production of silica refractory was canvassed and so the review extended to the production of silica from rice husk. This was treated in section 2.4. The manufacturing processes of silica refractory were reviewed in section 2.5. Section 2.6 is dedicated to reviewing the methods for refractory testing/ characterization, establishing reasons for the selection of the parameters investigated in this research. Reasons for and importance of using rice husk in this research are presented in section 2.7 titled "Why rice husk?" The chapter is concluded with section 2.8, which is a summary of the chapter.

2.2 Classes and Types of Refractories

The definition of ceramic refractory has been given in section 1.2. Ceramic refractory materials fall into different classes and types, depending on the application in which they are used. In the section that follows, an overview of the different classes and types of refractory materials is presented, with a view to pointing out the place of silica refractory in the industry.

Refractory ceramics can be classified on the basis of chemistry, end use and methods of manufacture as shown in Table 2.1, which is attributable to Gilchrist [7].

Table 2.1: Classification of ceramic refractory [7]

CLASSIFICATION BASIS	TYPE	EXAMPLE
Chemistry	ACID, which readily combines with bases	Silica, Semisilica, Aluminosilicate
	BASIC, which consists mainly of metallic oxides that resist the action of bases	Magnesite, Chrome-magnesite, Magnesite-chromite, Dolomite
	NEUTRAL, which does not combine with acids nor bases	Fireclay bricks, Chrome, Pure Alumina
End use		Blast furnace casting pit, insulating refractory
Special		Carbon, Silicon Carbide, Zirconia, Berrylia
Method of processing		Dry press process, fused cast, hand moulded, formed normal, fired or chemically bonded, unformed (monolithics, plastics, ramming mass, gunning castable, spraying)

Various types of refractories fall under these classes and for a broader understanding of the types of refractories available for use in the industries that require heat treatment, members of these classes need to be discussed further.

2.2.1 Alumina-Silica Refractories

These are sometimes referred to as alumino-silicates [3] and consist of the low alumina members (fireclay) and the high alumina members (sillimanite, mullite, bauxite-based and corundum. The members of this group are distinguishable by the percentage of alumina (Al_2O_3) that they contain. They therefore have a sub-classification as follows: fireclay, kyanite, mullite, bauxite-based and corundum.

2.2.2 Silica Refractory

Silica refractory (or Dinas) is a refractory that contains at least 93 percent SiO_2. The raw material is quality rocks (ganister) which may exist in many allotropic forms including quartz, cristobalite, tridymite and rarely as opal. Various grades of silica brick have found extensive use in the iron and steel melting furnaces and the glass industry. Some of the positive qualities of silica refractories are that they possess high fusion point (up to 1730°C) and high resistance to thermal shock (spalling) above 600°C [3]. The outstanding property of silica brick is that it does not begin to soften under high loads until its fusion point is approached and in fact, it can carry a load of about 1MPa within a few degrees of its melting point (1710-1730°C), according to Chesters [3]. Also, Kraplya *et al.* [4] have pointed out that this kind of behaviour contrasts with that of many other refractories, for example alumino-silicate materials, which begin to fuse and creep at temperatures considerably lower than their fusion points. Also to the credit of silica refractories, Kraplya *et al.* [4] mentioned that they have good flux and slag resistance coupled with excellent volume stability above 600°C.

2.2.3 Magnesites

From literature [1], magnesite refractories contain not less than 85 percent magnesia (MgO), an oxide which is chemically basic in nature. This group of refractories is made from naturally occurring magnesite ($MgCO_3$), from which the group derived its name. A magnesia refractory is defined by the American Society for Testing and Materials [1] as "a dead-burned refractory material consisting predominantly of crystalline magnesium oxide". Furthermore, the same ASTM defines "dead-burned" as "the state of a basic refractory material resulting from a heat treatment that yields a product resistant to atmospheric hydration or recombination with carbondioxide".

Like the alumina-silica refractories, the magnesite group of refractories has been classified and one of the classifications that have gained the widest applicability is the one done by the International Organization of Standards, ISO, which is shown in Table 2.2.

Table 2.2: ISO's Classification of Dense-Shaped, Basic Refractory Products [25]

Products	Limiting content of the principal constituents
Magnesite	MgO> 80%
Magnesite-chrome	8-18% Cr_2O_3 60-80% MgO
Chrome-magnesite	42-50%MgO< and 15-35% Cr_2O_3
Chromite	15-20% Cr_2O_3, 30-40% MgO
Forsterite	50-60% MgO and 30-40 SiO_2
Dolomite	30% CaO and 20% MgO

2.2.4 Special Refractories

There are several types of refractories grouped and termed 'special refractories'. They include the following: Zirconia refractories, Carbon Refractories, Oxide refractories (Alumina), and Insulating Refractory Materials (Insulating bricks, Insulating castables, Ceramic fiber, Calcium silicate, Ceramic coating).

The focus of this research is on silica refractories. Therefore, subsequent sections of this review would be devoted to the treatment of the subject of silica refractory research and development: its characteristic advantages, drawbacks, raw materials, the manufacturing process and the methods for characterization.

2.3 A Brief Survey of the Literature on Silica Refractory Research and Development: a Case for Silica Obtained from Rice Husk

This section provides information on the literature survey on the state of silica refractory research and development; the challenges therein and research attempts made so far to proffer solutions to the noted challenges.

2.3.1 Introductory Information

In all the industries dealing with the treatment of ores and other materials for the manufacture of metallurgical, chemical, and ceramic products, high temperature operations are involved in most of the processes employed. Such high temperature operations demand the use of specialized equipment referred to as furnaces. The inner chambers of furnaces are often lined with some materials of ceramic classification called refractory, to protect the external construction materials from excessive heat. The definition of refractory has been given in section 1.2. Technologically speaking, refractory materials generally refer to the materials employed for the construction of the chambers of furnaces, flues, crucibles, *etc*, which are used in high temperature operations, to ensure such equipment are resistant to the abrasive and corrosive action of solids, liquids or gases (including slag) present therein [3, 26].

Silica (SiO_2) is the oldest refractory used by man and it is available worldwide. It is regarded as the most abundant mineral found in nature, being present in sand across the earth surface [5]. Silica exhibits polymorphism with some of the polymorphs existing as either crystalline or non-crystalline (amorphous) in nature. Explaining the differences between these two states in which silica could exist, Smith [27], stated that the term "crystalline" refers to when the arrangement of atoms in the material is well oriented or ordered in both short- and long-range in three-dimensions, and a discrete sharp X-ray powder diffraction pattern could be obtained from it when investigated. On the other hand, the use of "non-crystalline" is associated with materials that may contain some short-range order, but lack long-range order in three-dimensions and produce X-ray powder diffraction patterns composed of broad maxima, which may or may not be mixed with sharper maxima. This difference in structure affects the property behavior of the products made from silica.

It is reported in literature [3] that silica refractory has very good refractory properties. These good properties include amongst others, high fusion point (up to 1750°C), high resistance to thermal shock (spalling) above 600°C and their high refractoriness under load. Silica refractory (or Dinas) is defined as one that contains at least 93 percent SiO_2. The major source of the raw material used in silica refractory production is quality rocks. This raw material exists in many allotropic forms, predominantly quartz. Various grades of silica brick have found extensive use in the iron and steel melting furnaces and the glass industry.

One of the outstanding properties of silica brick is that it does not start to soften under high loads until its fusion point is approached and in fact, it can carry a load of about 1MPa within a few degrees of its melting point (1710°-1730°C), as stated in [3]. And according to Kraplya *et al.* [4], this behavior contrasts with that of many other refractory, for example alumino-silicate materials, which begin to fuse and creep at temperatures considerably lower than their fusion points. Kraplya *et al.* [4] also mentioned other advantages of silica bricks to include flux and slag resistance and volume stability above 600°C. Apart from these, silica refractory has a tolerable thermal conductivity, such that it does not necessarily require the use of back-up insulation during furnace construction, which makes for furnace chamber optimization.

It is therefore not surprising that much research was carried out in silica refractory development in the period ranging from 1913 to 1990, which has been termed in this survey as the *Early Research Era*. However, the research pace greatly slowed and the theme changed; they no longer addressed issues and questions that were raised in the early research era, as the survey shows. Rather, there appears to be an abandonment of silica refractory (their use now only being restricted to the roofs of furnaces and ovens) for, what literature presents as better performing refractory. The impetus for this research is founded on the belief that it is possible to continue research on silica refractory in order to make them more attractive than ever, tapping from the advances in science and technology, especially the great promise nanotechnology presents.

The aim of this brief review is to highlight the problems and the conclusions elucidated in early works in the field of silica refractory research and development; assess the current state of research (its theme), in order to ascertain the extent to which the drawbacks observed and reported in earlier research have been addressed, with the goal of mapping a future research course. The survey is era-divided and period defined: *Early Research Era* (1913-1990), *Current Research* (1991-2013) and *Future Research Directions-a case for rice husk ash (RHA).* Owing to the volume of work and amount of literature available on silica and silica refractory research and development, it was necessary to define a realistic scope for this survey. Consequently, the review briefly points out the gaps identified in silica refractory amongst researches that were carried out from 1913 to 1990, which have direct bearing on silica refractory development; that is, works that have to do with structure-property relationship, manufacturing process parameters and techniques as well as refractory characterization. The review then methodically assessed the direction and theme of the work contained in the current research (1991 to 2013), in order to chart a course for future research directions.

2.3.2 Early Research Era (1913 to 1990)

A review of the theme and trend of current research (1991 to 2013) would be baseless if attempt is not made to consider the research findings or results of the previous era (1913 to 1990), so as to know what research gaps need attention. Therefore, the main purpose of including this era in this review is to establish a baseline research direction and gaps, in order to assess how well current research has addressed the questions raised, thus laying foundation for further or future research directions. To comprehensively do this, the following grouping is made, depending on the research focus: (a) Silica Structure and classification, (b) Sintering Behaviour of Silica Refractory and the attendant property changes and (c) Silica Refractory Manufacturing parameters and Techniques. Major conclusions in terms of research gaps in these enumerated areas would be considered, in reviewing research in the early era (1913 to 1990).

2.3.2.1 Silica Structure and Classification

Several researches that dealt with this area are available in the literature [28-36]. These researches have been able to establish the structure and polymorphic classes of silica. Major research in this field began with Fenner [28], who worked extensively on the phase stability of silica. Though, the veracity of his work has been questioned by Stevens and coworkers [37], it forms the bedrock of silica refractory (based on crystalline silica- quartz) development and it is still widely cited.

The investigations contained in [28] first revealed the fact that when heated, silica undergoes some phase transformations and went ahead to establish the inversion temperatures as follows:

$$\text{Quartz} \xleftrightarrow{870^\circ\text{C}} \text{Tridymite} \xleftrightarrow{1470^\circ\text{C}} \text{Cristobalite}$$

Sosman [38] and Floerke [30] have given a vivid account of the interaction of other phases of silica, their stability and existence criteria, which are best depicted by Figure 2.1.

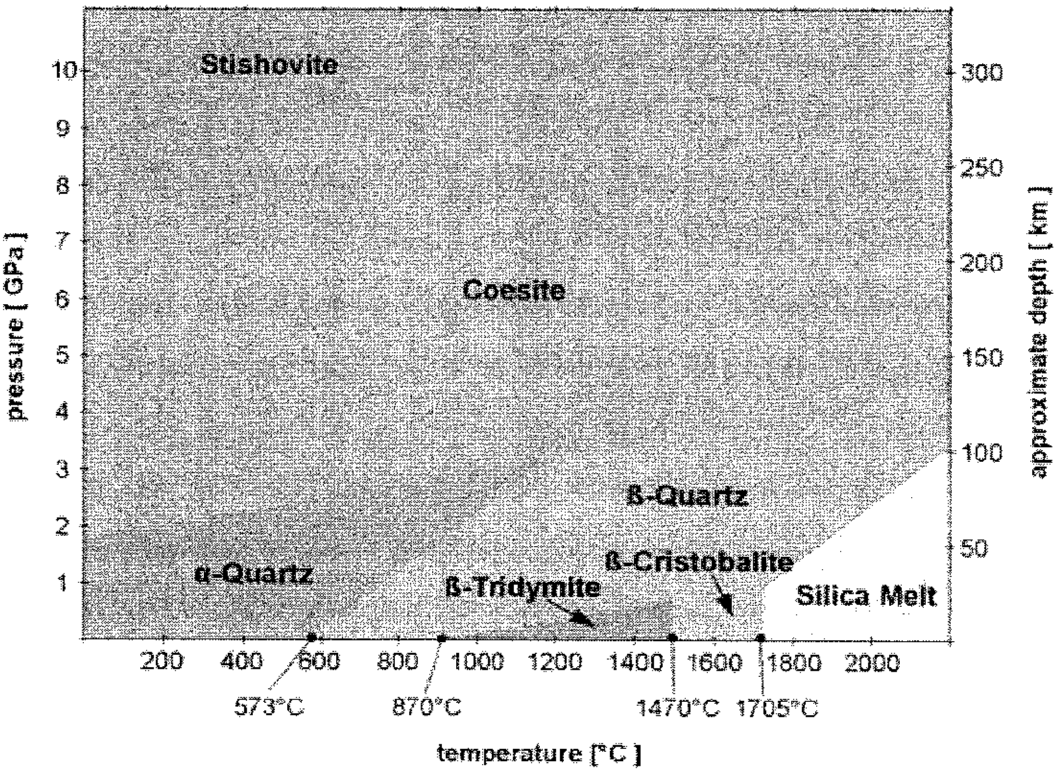


Figure 2.1: Phase diagram of silica, SiO_2 [39].

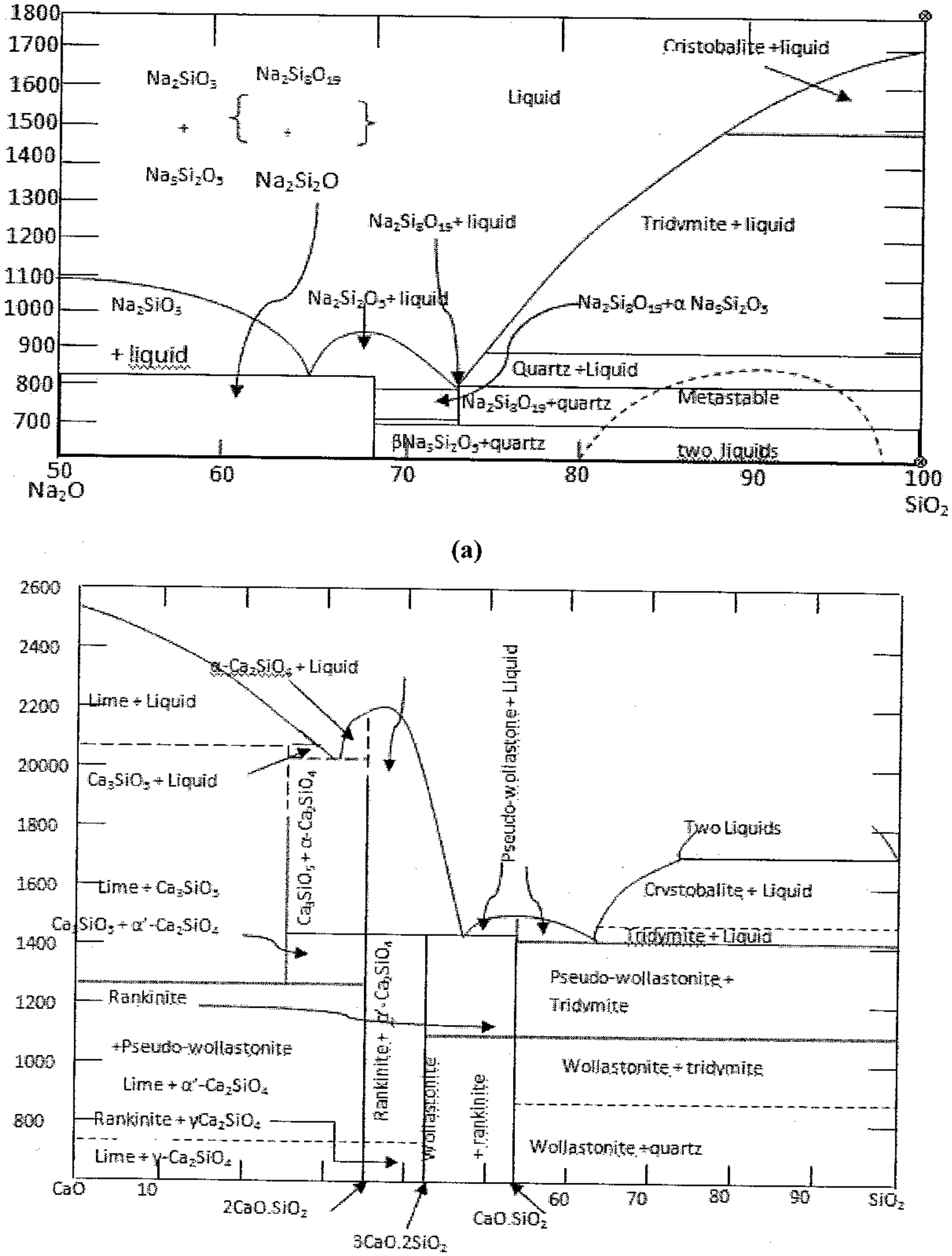
Sosman [38] was able to point out seven distinct polymorphs of silica (SiO_2): quartz, cristobalite, tridymite, coesite, stishovite, lechatelerite (silica glass), and opal, with the latter two declared as amorphous[40, 41]. Also, significant early contributions were made by Floerke [42], who hypothesized on the basis of XRD that opals are disordered intergrowths of cristobalite and tridymite and by Jones *et al.* [43], who determined that gem-quality opals are 3-dimensional arrays of amorphous silica spheres.

2.3.2.2 Sintering Behaviour of Silica Refractory and the Attendant Property Changes

The major conclusions of the researches in this section are the establishment of the phases or polymorphs of silica (at least 22 polymorphs were given) and the conditions and criteria for their formation or existence. Also, they were able to point out that not all silica polymorphs are crystalline in nature; some like opal, are amorphous. As could be seen from Figure 2.1, during silica refractory calcination, there is a change of phase as silica refractory is heated past the temperature range of 570^0C to 600^0C, which is the inversion temperature range for the transformation: α-quartz to β-quartz. Sosman [38] observed that there is a volume change of about 1.35 percent, which gives rise to a deleterious phenomenon- shattering of the refractory bricks. He attributed this shattering phenomenon to the sudden expansion of the silica refractory bricks as a result of the phase transformation. For this reason, heating a furnace lined with silica refractory past this temperature range has to be gradual and pursuant to this effect, Gilchrist [7] suggested a firing rate of not more than 10^o per hour, if the shattering phenomenon in silica refractory bricks may be minimized. Consequently, longer periods are required to soak the furnace up to the working temperature, resulting in great energy demands and losses, as well as man-hour wastage.

Lynam [44] gave a concise history of silica refractory bricks manufacture. In his [44] presentation, it was pointed out that based on research findings; it was safe to recommend a maximum lime content of 2%, firing to complete inversion (to allow the formation of tridymite) and slow cooling to avoid cracking in the manufacturing process of silica. He explained that this was necessary in order to obtain bricks with good dry strength. It is worthy of note that it was Dale [45], who first extensively worked on the effects of lime addition on the property changes that occur during firing of silica refractory bricks, though such details are not presented here. Holmquis [46]reinvestigated the conditions under which tridymite becomes a stable phase. He explained that when quartz is heated with 2% alkali oxide, tridymite formed directly at 872° to 898°C with Na_2O, at 883° to 902°C with K_2O, and above 1005°C with Li_2O. Cristobalite occurred as an intermediate phase above 893°C with Li_2O, above 898°C with Na_2O, and above 902°C with K_2O. His investigations were further developed by Muan and Osborn [47]. The results of these investigations showed that the formation of tridymite can be strictly a solid-state process. The results of this work led to the construction of the phase diagrams of the binary systems: Na_2O-SiO_2 and CaO and SiO_2, as shown in Figures 2.2 (a) and (b), the very foundations of the determination of the quantity of the alkali oxides in silica refractory production process.

The importance of these works lies in the fact that tridymite phase could be made to form and even stabilize in a silica system. This fact is employed in the manufacture of silica refractory, by the deliberate addition of CaO to the mixture during processing. Tridymite has been described [38] as the polymorph of silica with needle-like structure, capable of interlocking when formed at this elevated temperature. The usefulness of this interlocking character is that it imparts mechanical strength on the sintered refractory and most often, the higher the percentage of tridymite formed in the refractory body, the better the mechanical strength.



(a)

(b)

Figure 2.2: The binary system of (a) Na_2O-SiO_2 (b) CaO-SiO_2 phase equilibrium diagrams (adapted from [48])

The phase diagrams shown in Figures 2.2 (a) and (b) can also give an idea of the type of alkali oxide that is needed for a given application. For instance, in glass manufacture, where low melting temperatures are preferred, users would smartly go for Na_2O instead of CaO, which gives a higher eutectic. These phase diagrams thus serve as good guides.

2.3.2.3 Silica Refractory Manufacturing Techniques

Early researches on the determination of the parameters for the manufacture of silica refractory were carried out in [49] and [50]. McDowell [49] studied the effects of permanent crystal changes in silica refractory on being heated to temperatures usually attained in manufacture. He also studied the effects of such changes on the strength of the refractory and its spalling character, when rapidly heated or cooled. He was able to establish a relationship between tridymite formation and improved mechanical strength of the refractory. From here, Ross [50] took over the study and investigated the properties (especially physical and mechanical) as well as the materials used in the manufacturing process. He recommended that silica refractory bricks be given an extended heating period (what could be termed soaking or dwell time) between the temperatures of 1250°C and 1350°C, to enable the formation and retention of good quantity of tridymite that would impact positively on the mechanical properties of the products.

Hugill and Rees [51] worked on the effects of particle size on the porosity of silica refractory and recommended that in order to achieve a high bulk density, a mix of this proportion: 45% coarse, 10% medium and 45% fine was necessary. Some other researchers also carried out works on silica refractory manufacture.

All of these details, put together, form the bedrock of silica refractory manufacture till date. The authors are of the view that science and technology has grown, perhaps out-grown these procedures and improvements are required and necessitated. Nanotechnology presents great potentials in all fields and could be employed in this field of refractory development to achieve greater performance in service, of silica refractory.

2.3.3 Current Research Era

In this section, an assessment is made of the current research theme followed by a comparison of the theme with the results of the early research era. Literature directly related to silica refractory research and development in this era is quite sparse. Even the ones that were done [9-11, 13, 52] merely helped in corroborating the findings of the early research era. There were no major milestones reported. They have used the same style as the early researchers, only testing new materials and have therefore, not come up with better ways of producing silica refractory, with superior performance. Specifically, the great challenge observed in silica refractory- very poor spalling resistance between the temperatures of 570° and $600^{\circ}C$, is yet to be circumvented. There is not a record to show how the optimal value of binder (to impart green strength) used in the manufacturing process could be determined. It is reported in the literature [2, 3] that pressure is applied to the bricks after batching and mixing, but how much of this pressure is suitable for the right level of porosity, bulk density and thermal conductivity is not reported in any literature, at least in this era. In terms of raw materials, only [9, 10] reported the use of local sand for brick production and characterization.

However, current research [15, 16, 53-67] has shown that there could be an alternative source of silica: rice husk ash (RHA) rather than the earth. This holds good promise for earth conservation and improved income for the populace in communities where rice is grown. Therefore, future research should take this direction.

2.3.4 Future Research Directions and a Case for Silica from Rice Husk

Raw materials have been and will continue to be important to the refractory industry because they affect batching and mixing, product quality, properties, innovation and advancement and profitability [14]. This statement underscores the importance and need to pay attention to the source of silica for the manufacture of refractory. It was mentioned earlier that the source of silica for refractory manufacture has always been from ganister and silica rock, rich in quartz. Davies [8], in reviewing British sources of silica posited that for the production of high quality silica refractory bricks, raw material should contain at least 97% SiO_2 (quartz) and less of alkali bearing silicates. In [8], there is a foul cry against the fast depletion of (progressive exhaustion, without renewal) silica refractory raw materials and a recommendation that research and development should move in the direction of alternative materials, if growth in the industry was to be sustained. Chesters [3] reported that the use of opaline silcrete after the world war gave rise to bricks of superlative performance, called super-duty silica bricks. It is therefore, not out of place to insist on research that could identify renewable sources of silica, especially those with opaline structure. With works reported in [42] combined with that in [43], it becomes clear that it is possible not to encounter β-tridymite during calcination of opal silica. What this hypothesis suggests is that it is possible to produce silica refractory from opline sources, without witnessing the deleterious shattering phenomenon associated with bricks from quartz sources.

Many researchers [15, 16, 53-67] have pointed to the fact that rice husk is an alternative rich source of silica, howbeit, amorphous (opaline) silica. This fact has been covered widely, although, not in direct relation to the production of silica refractory. While some have used RHA as adsorbent [53, 57], some others have used it as a substitute for cement or pozzolan [16, 54, 58, 63, 64, 66, 67]. Only a few have tried to use RHA for refractory or ceramic production [59, 62, 68]. Many of the research [56, 61, 65, 69] deal with physical and chemical characterization of the ash. Specifically, Kapur [68] studied the feasibility of refractory production from rice husk ash, viewing the subject from the realms of manufacture, properties and usage of a spectrum of low to high temperature thermal insulations and insulating refractory. Among the compositions he considered are namely: (i) Calcium ferrite bonded porous silica refractory: (ii) Sodium silicate bonded porous silica refractory; (iii) Fired and chemically bonded forsterite insulating refractory; (iv) Hydraulic setting calcium silicate/silica thermal insulation. This had laid a good foundation for future research aimed at the use of RHA for the production of silica refractory.

To boost the study, the work by Liou [61] comes handy, wherein he prepared and characterised submicron size silica from RHA. He however, failed to direct it at any specific material application. From the results [61], it is believed that indeed, it would be highly productive to develop the production of refractory from submicron size silica obtained from RHA. If this development is undertaken, it would result in a new work and it would therefore be necessary to optimize the production process for refractory manufacture using submicron size silica obtained from RHA, since such an endeavour has not been discussed in any literature. It is therefore necessary to investigate the physical, thermal and mechanical properties of refractory produced from submicron size silica obtained from rice husk ash. For example, since it has been established that alkali oxides could aid in the formation of tridymite on sintering silica, there is need to establish what the optimal value of the alkali oxide is (in terms of quantity or percentage), in silica refractory production process for submicron size silica from RHA. What binders are effective for green strength improvement in the refractory and in what optimum quantity, the sintering temperature as well as dwell (soaking) time, also need to be determined. Other research questions for future research include: what are the magnitudes of the dilatometric changes that occur in silica refractory produced from rice husk ash and at what temperatures? What is the nature of the phase changes that occur alongside and at the temperatures at which these dilatometric changes are observed? What consequences, if any, do these dilatometric changes have on structural stability of the refractory? At what rate is heat transferred through the refractory and as well, what is the refractoriness and working temperature of rice husk ash silica refractory and what mechanical properties do they exhibit at high and low temperatures?

2.4 A critical Assessment and New Research Directions in Rice Husk Silica Processing Methods and Properties

2.4.1 Introductory Information

It was estimated that world paddy production in 2010 was over 700 million tons [70]. Around 22% of the paddy mass is husk [71], which consists of opaline silica in combination with a large amount of a phenyl propanoid structural polymer called lignin, hemicellulose and cellulose [72]. Consequently, over 154 million tons of rice husk were generated in 2010. The average composition of rice husk is given in Table 2.3.

Table 2.3: Composition of rice husk [73]

Constituent	Composition (%)
Cellulose	35
Hemicellulose	25
Lignin	20
Crude protein (N x 6.25)	3
Ash	17 (silica 94%)

When rice husk is incinerated, it generates between 17-20% ash, made up of about 87-93% opaline silica and other metallic oxide impurities depending on the source of the husk. This kind of high percentage of silica intermingling with plant fibres is quite rare in nature. The close intermingling of silica and lignin has two consequences: the rice hull is not only made resistant to water penetration and fungal decomposition, it is also resistant to the best efforts of man to dispose it. Since the hull represents an average about 22% of the rough harvested weight of rice (paddy), our planet is speedily being filled up with an abundance of this scaly residue. Juliano [74] has also pointed to the fact that of all cereal by-products, the rice hull has the lowest percentage of total digestible nutrients (less than10%). Also reporting a drawback of rice husk usefulness, Olivier [72] stated: "Nowhere could we ever find a cereal by-product so low in protein and available carbohydrates and yet, at the same time, so high in crude fibre, crude ash and silica." This statement corroborates the fact that rice husk is not even good as a fodder for animals. Though some organic products such as furfural have been produced from rice husk [75], its richness in ash and silica has been of great research interest because many value-added products could be obtained from this agro-waste.

When rice husk is incinerated, two types of products could result, depending on whether the combustion was complete or incomplete. When combustion is complete, white rice husk ash (WRHA) and when combustion is incomplete, pyrolized rice husk (CRH) is produced. In either of these forms, rice husk has found some applications. Among the uses reported are: as a good pozzolan in cement industry [16, 66, 76-80].

Other products like aerogels [81, 82], SiC [83, 84], porous carbon [85], zeolites [86], cordierite [87], *etc*, have been prepared using rice husk silica. An earlier work reported the indirect use of rice husk in making insulating refractories [88, 89]. These uses are related to the processing route or method used, which often affect the product characteristics. For example, research by Hamdan *et al.* [90] has shown that different methods of preparation of rice husk silica produce different morphology, structure and reactivity.

Although, some authors have carried out reviews on this subject, it is noteworthy that science and technology as well as research and development are not static. As a field develops, new findings result in the need for an extension in the reviews, especially when such previous reviews are up to five years old. The latest reviews on this subject are the works of Sun and Gong [91] and that done by Chandrasekhar *et al.* [92], which were published in 2001 and 2003 respectively. Since then, there has not been another review again carried out on the subject, even though there have been dramatic developments in technology. This review is therefore, another attempt to again review the research depth and directions of the processing methods, characteristics and utilization of rice husk silica in these inter-twinning years, and in so doing chart a research course for research and development in the field. In a nut share, the review presents critical review of literature, assessing the current production facilities and processes in the field, the influence each process has on the product characteristics, culminating in a tabulated selection guide to process-product match and the review ends by making case for the process currently being developed, which is called the hydro thermo-baric process. It is our hypothesis that the process being developed would inexpensive and would be versatile as regards the effects it would have on the quality of rice husk silica it produces, by varying the process parameters.

2.4.2 Composition of Rice Husk Ash

Several authors have reported different values for the composition of rice husk ash as shown in Table 2.4. It is inferable from Table 2.4 that the composition of rice husk silica ash varies and is largely dependent on many factors, including, but not limited to agricultural practices like the use and types of fertilizers employed during rice cultivation and or climatic or geographical factors, resulting in the variability of the constitution of rice husk. Thus, depending on the geographical locations, different authors have published different values for the composition of rice husk as shown in Table 2.4. Methods used to evaluate the compositions quoted are indicated on the table.

Table 2.4: Composition of rice husk ash by different researchers

Composition	Percentages of the constituents as per authors in square brackets and method used outside the brackets			
	[93] XRF	[94] ICP	[95]*	[**] XRF
SiO_2	91.56	91.5	87.79	91.25
K_2O	4.76	1.23	1.69	3.829
P_2O_5	-	0.30	4.74	2.45
CaO	0.78	0.57	1.24	0.875
SO_3	0.29	-	-	0.661
MgO	-	0.30	1.59	0.573
Al_2O_3	2.36	0.62	0.4	0.18
Fe_2O_3	0.11	0.42	0.37	0.0866
MnO	0.07	0.04	-	0.0726
Rb_2O	-	-	-	0.0143
ZnO	0.01	-	-	0.0111
CuO	0.01	-	-	-
Na_2O	-	0.18	-	-
LOI	N.D.	3.05	2.08	N.D.

* Method not specified. ** From the authors' laboratory; N.D. = Not determined

From the Table 2.4, it is clear that though the composition of rice husk may be dependent on several factors (which are mentioned in the above paragraph), the percentage of silica (SiO_2) within the ash ranges between 87 and 93%. Other researchers [96] have reported samples from USA to contain trace amounts of titania (TiO_2). Due to this compositional variation therefore, the suitability of rice husk silica for any given application will be largely dependent on the purity level needed and if this level of purity is not met from the beginning for a given application, then purification process would be carried out to reduce or eliminate the unwanted impurities. Several methods that have been used variously by different authors to produce silica from rice husk are discussed next.

2.4.3 Processing of Silica from Rice Husk

Different processes have been used by different researchers to obtain silica from rice husk. The following discussion reviews these processes, highlighting their advantages and disadvantages.

2.4.3.1 Direct Incineration without Pre-treatments

Some workers [19, 97-102] have directly incinerated rice husk to produce silica of varying purity, with or without the use of pre-treatments. In the overall process, the temperature of incineration, holding time and pre-treatment techniques employed affect the character, especially the surface area and brightness (whiteness) of the silica produced. The transformation of raw husk to clear white, grey or pale grey ash is critically dependent on the temperature of incineration [98]. For instance, temperatures between 300°C and 450°C would only transform fresh rice husk (Figure 2.3(a)) to pyrolized husk (Figure 2.3(b)), while temperatures between 500 and 650°C produce white or grey ash (Figure 2.3(c)), depending on soaking time, that is the duration for which this incineration was allowed to proceed at the stated temperature range.

Figure 2.3: States of rice husk (a) fresh (b) pyrolized (c) completely incinerated

As the incineration temperature increases, there appears to be some phase changes that accompany it. The findings of research regarding these phase changes will be discussed in section 2.4.4, which discusses properties of rice husk silica. However, it is worthy of note that rice husk silica produced at temperatures between 500 and 650°C with incineration holding (soaking) times of between 2-one-half and 6 hours are considered ideal to convert rice husk into white amorphous silica, whilst, crystallinity sets in when incineration temperatures increase beyond 700°C and the quantity of the operational phase, whether cristoballite or tridymite, is dependent on the applicable temperature range and the impurity level in the rice husk. Also, it is reported [98] that the incineration temperature grossly affects the surface area and hence, the reactivity of silica produced from the direct incineration process.

Direct incineration of rice husk can be accomplished in the open air as reported by Hamdan *et al.* [90] or in a muffle furnace as was done in [24]. Another method used by some researchers [19, 101, 102] is the fluidized bed combustion technique to produce rice husk silica, even though the reported percentage purity was not more than 95%. So whether in static or flowing air, complete incineration could be achieved, howbeit, with some varied effects on the properties of the silica produced. Another technology [103] was developed in India (Figure 2.4), for the direct incineration of rice husk and it works like a TORBED reactor, with details described elsewhere [104].

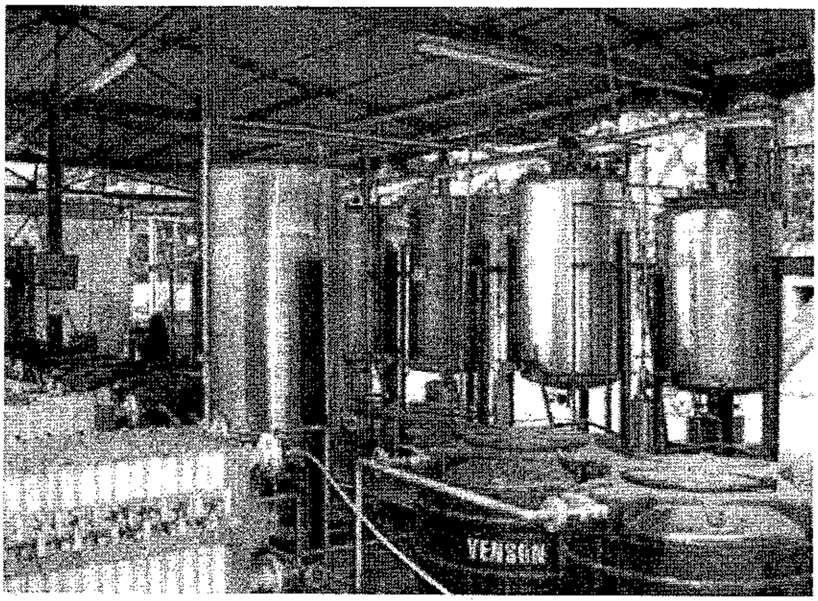


Figure 2.4: A pilot plant for rice husk incineration in India [103].

2.4.3.2 Pre-Treatment Effects on Silica Production from Rice Husk

One of the reasons why it has been difficult to obtain silica with purity in excess of 97% from rice husk by the direct incineration process is a consequence of the effects of the metallic impurities the husk contain. For instance, it has been reported by Chandrasekhar *et al.* [105] that alkali oxides, especially K_2O impart black colour on the particles. Some explanations to support this phenomenon is that there exists a strong interaction between alkali oxides, especially oxides of potassium and sodium, contained in rice Husk and the silica therein, such that they can result in the surface melting of SiO_2 particles and accelerate the early crystallization of amorphous SiO_2 into cristobalite, as implied by research results [23, 97, 106, 107]. This is one of the reasons why Kalapathy *et al.* [108], could not achieve purity of up to 98% even after 14 hours of their sol-gel treatment of rice husk ash, with bases and acids. This surface melting of these oxides on the silica grossly reduces the surface area, thereby reducing the reactivity of the particles. For this purpose, it is often necessary to use some pre-treatment methods (which can either be done through acidic or basic medium), to reduce or remove metallic impurities, in order to increase the chances of obtaining silica of higher purity and surface area than is achievable in the direct incineration method.

Three main pre-treatment methods have generally been used in the production of high purity silica from rice husk. These are acid leaching, basic pre-treatment and microbiological pre-treatment, usually in combination with some acids. These processes are discussed as follows.

Several kinds of acids, both mineral and organic have been reported to be used to pre-treat rice husk before other value adding processes such as incineration are begun [23, 99, 100, 105, 107, 109]. However, HCl has proved to be the most effective in removing metallic impurities from the husk and so, it is by far the most widely used. Chakraverty *et al.* [110, 111] found that the leaching of rice husk in 1 N HCl was effective in substantially removing most of the metallic impurities. Other researchers [105] used organic acid and compared results obtained with those obtained by using other different mineral acids in pre-treating rice husk and concluded that HCl was better. They gave the order of efficiency to be $HCl > H_2SO_4 > HNO_3$. However, Umeda and Kondo [112] reported a very high purity (>99.5%) silica from rice husk, while pre-leaching it with citric acid.

While acid leaching affects the chemical composition of the husk, it does not however, affect the structure- whether crystalline or amorphous, of the silica. Thus, change of phase (from amorphous to crystalline) is not affected by the pre-treatment method employed in the production of silica from rice husk. A very vivid insight into this dynamics is presented in the research report of Real *et al.* [23]. In their research, they found that the preliminary leaching of rice husk with a solution of HCl before incineration at 600°C, if properly done, could result in high purity silica (approximately 99.5%) with a high specific surface area (approximately 260m^2/g). They indicated that the high surface area silica produced is unaffected even after being heated at 800°C. They were able to prove that it was the treatment before incineration that was effective as the test results showed that if the leaching with HCl was performed on the white ashes obtained from incineration of untreated rice husk at 600°C, an amorphous silica with the same purity would be obtained, but its specific surface area decreased to as low as 1 m^2/g. High surface area enhances the reactivity of silica from rice husk. These researchers [23] later explained the kinetics of this drastic change in surface area, attributing it to the interaction between alkali oxides, specifically, K_2O and SiO_2.

Other acids, such as H_2SO_4, HNO_3, or their mixture, have also been used in acid pre-treatment [56, 99, 107, 110, 113, 114]. The general leaching effects of H_2SO_4, HNO_3 and HCl are similar, but HCl leaching of rice husk is superior to H_2SO_4 and HNO_3 leaching in removing the metallic ingredients [110]. Some researchers [107, 108] have also attempted chemical post-treatment of incinerated rice husk using HCl, the results were however, inferior to those of pre-treatment procedures.

Some alkalis, such as NaOH and NH_4OH, have been used to pre-treat rice husk [56, 100, 113]. However, the effects of alkali pre-treatment are not as obvious as the effects of acid pre-treatment, but the results, especially those of [24] are too dismal to be considered for any meaningful application.

Researchers [56, 115] have also attempted the use of microbial fermentation as a pre-treatment for rice husk, in order to obtain silica. Although the results are similar to those obtained from acid pre-treated processes, the method is disadvantageous in that the time required for the fermentation process to complete is too long, making it unfeasible for practical applications.

2.4.3.3 Hydrothermal Method

Hydrothermal synthesis has been defined as a process that utilizes single or heterogeneous phase reactions in aqueous media at elevated temperature (T>25^{0}C) and pressure (P>100 kPa) to crystallize ceramic materials directly from solution [116]. As stated in the introduction, rice husk contains organic compounds and oxides of metals. Under high temperature, high pressure, and acidic or basic media with strong oxidation activities, the organic compounds can be decomposed, and the trace metals can be turned into soluble ions; then, silica can be obtained. This processing method can achieve purification of the silica from the husk, with only the use of water. However, achieving complete dissolution of the organic matter in the rice husk is a task that is near impossible. So, practically speaking, this process still requires the incineration step, though the soaking time may be less compared to incinerating the untreated or pre-treated rice husk. The method does not affect the amorphicity of the silica in rice husk. Some acids with strong oxidation activities such as H_2SO_4 and HNO_3 are used and sometimes H_2O_2 is also used as the oxidative medium. Among researchers that have used this method are Mochidzuki *et al.* [93] and Wu [117].

2.4.3.4 Other Methods

Researchers [118, 119] have reacted pyrolized rice husk with Na_2CO_3 solution in the proper ratio for 3 h, followed by incineration step at temperature range between 600-650^{o}C for varied soaking times between 3 and 7 hours to obtain silica. The silica made from this method has good reinforcing properties in rubber. In an earlier review [91], it is reported that this method involves the mixing of rice husk ashes with NaOH to produce sodium silicate and then, the sodium silicate would be reacted with NH_4HCO_3, $(NH_4)_2SO_4$, or H_2SO_4 to produce SiO_2.

2.4.4 Critical Appraising Remarks of the Processing Methods

The processing methods involved in the production of rice husk silica have been reviewed. Apart from the production done with the TORBED incinerator or the fluidized bed combustion, all other methods are mostly done on a laboratory scale. Though the output from the TORBED and fluidized bed combustion is high, both processes do not improve the purity of the silica obtained. One other problem with these two processes is that the temperature under which the rice husk incineration takes place in these two processes is beyond 700°C, the threshold temperature for the produced silica to transform from amorphous to crystalline state. The quality of the silica obtained from the fluidized bed combustion or the TORBED incinerator is normally below 93%, which restricts its application to non-chemically sensitive areas like cement and concrete admixtures, where high purity silica is not essential. For these two reasons, both the TORBED and fluidized bed methods cannot meet the requirements in terms of purity and structure (amorphous) for silica refractory manufacture.

Their capability to produce high purity RHS notwithstanding, the other methods- acid leaching and the sol-gel methods- have their draw backs too. As stated earlier in the problem statement, one of these problems is that the chemicals used in the processes are highly corrosive, with dangerous and environmentally unfriendly by-products. Laboratory use of these methods requires extra precautions and high investment and maintenance costs on HSE (health, safety and environment) equipment and procedures. Secondly, the time spent on the processes to obtain purified silica is much, as shown in the Table 2.5

Table 2.5: A comparison of the processing times of different processes

Author	**Method**	***Processing time (hours)**			**Total time (hours)**
		Pre-treatment	Post-treatment	Others	
Yalcin and Sevinc [24]	Boiling in 3% v/v HCL	2	-		2
Umeda and Kondoh [112]	Leaching with citric acid at boiling point	1	-	¼ water rinsing	$1^{1}/_{4}$
Nittaya and Apinon [120]	Precipitation method by boiling in 5N NaOH for hours (sol-gel)	3	-		3
Kalapathy *et al.* [108]	Precipitation and back-titration using concentrated acids and bases (sol-gel)	-	1	20	21

*Times shown are those involved in impurity removal from either the raw rice husk or its ash.

So, even though many authors [15-17] concluded that rice husk is an excellent source of high-grade amorphous silica, the speed of the processes of acid leaching and sol-gel methods does not make them a viable option in selecting anyone of them as a process that would produce silica for an industry, like silica refractory manufacture, that requires high volume of the product. For this reason therefore, it is necessary to evolve a system that can both produce high purity silica at volumes of production capable of supporting industrial growth. This is what led to the development of an alternate method for the production of high purity RHS. The developed process is termed hydro thermo-baric (HTB) process for fast production of high purity silica from rice husk. The principle behind this new process is discussed in section 2.4.5.

2.4.5 Principles of the HTB Process

This section describes the basic theory and simplified design of the hydro thermo-baric process reactor, as published in our article [121]. The Hydro thermo-baric (HTB) purification, like the solvo-thermal or ammono-thermal process, is a type of hydrothermal process, that utilizes single or heterogeneous phase reactions in aqueous media at high temperature ($T > 516K$) and pressure ($P > 3MPa$) to cause leaching or solutionizing of oxide impurities as well as degradation of organic compounds of rice husk. While in hydrothermal processes, different oxidizing agents such as H_2O_2 or H_2SO_4 are used to cause oxidation in water, the HTB process utilizes only water as its aqueous medium. The theory behind the process in which water is the sole aqueous medium, is that water autoionizes forming hydronium (or hydrated proton or protonized water) (H_3O^+) ion as well as the hydroxyl (OH^-) ion, thus behaving like an acid-base system, capable of reacting with basic and acidic oxides. This process reduces or can leach away the metal impurities of the rice husk to levels that are compatible with and acceptable in several industries utilizing silica as raw material for manufacture. Also, the organic components (the hemi-cellulose, cellulose and lignin) of the husk are expected to be converted to sugars and acids or other organic compounds and solvents (to a large degree). This leaves only small portions of these cellulosic components in the post-treatment rice husk, thus reducing the incineration time, smoke generation, and rigours required to obtain the silica from the husk.

2.4.6 Properties of Rice Husk Silica

In this section we examine the properties of rice husk silica, one after the other and see how the production process employed affects such property.

2.4.6.1 Structure

Different research reports present the structural state of rice husk and show that it is dependent on the processing temperature. Often, the structure of the silica is investigated by X-ray diffraction (XRD) and the state is revealed by the shape of the difractogram obtained. The studies done by Hamdan *et al.* [90] show that for various temperature ranges, silica rice husk can exist in either the crystalline or amorphous states as shown in Figure 2.5.

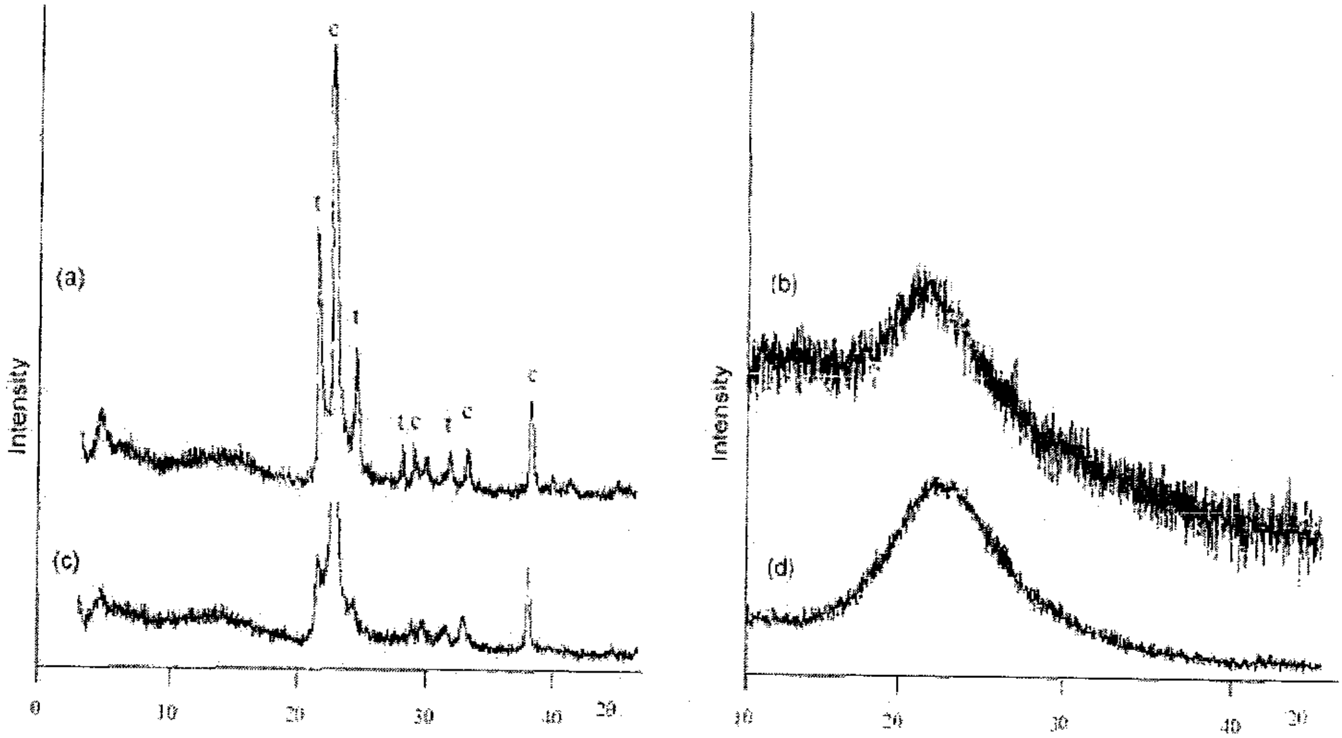


Figure 2.5: X-ray diffrctograms of rice husk silica processed at different temperatures [90]

Figure 2.5(a) is the diffractogram of rice husk silica processed through open field burning, where temperatures can reach 900°C, while Figure 2.5(c) represents samples prepared in furnace at 1000°C for 4 hours. Figures 2.5(b) and (d) are samples prepared in muffle furnace at 700°C for 4 hours and hydrothermally extracted silica respectively. As is evident from the diffractograms, only samples represented by Figures 2.5(b) and (d) are amorphous, while the other two are crystalline in nature with the formation of crystobalite and traces of tridymite. These findings are in total agreement with the work of Kapur [98], who studied the structural behaviour of silica within the temperature range of 400-1500°C. He explained that at combustion temperatures above 900°C, the SiO_2 in rice husk ash (RHA) consisted of cristobalite and a small amount of tridymite. Other researchers [122] have also reported similar results. Thus, it is a conclusive opinion that to obtain amorphous silica from rice husk, processing temperature should not exceed 700°C, as phase transition to crystalline structure of crystobalite would soon follow, although, no specific temperature has been reported for this transformation. It is not yet clear if some of the inversion temperatures for quartz would hold true for opal; thus, research of greater depth is still required to investigate these temperatures of inversion with respect to rice husk silica.

2.4.6.2 Surface Area and Pore Size and Volume

Surface area and pore volume of rice husk silica is dependent on the processing temperature, since this affects the surface melting of the silica due to the presence of alkali oxides. Different values of surface area and pore volume have been reported in literature [61]. Kapur [98] reported an initial increase in the surface area from 60 m^2/g to 80 m^2/g when the husk was incinerated at 350 °C and at 600 °C respectively. He explained that this increase was perhaps due to the burn-off of the residual carbon and the opening of new pores. His work further revealed that between 700 and 900°C, a sharp drop occurred in the surface area from 40 to only 1 m^2/g, as a result of the alkali metal oxides.

2.4.6.3 Morphology, Particle Size and Chemical Species

It is a generally accepted fact that indicated that SiO_2 which is formed by incinerating rice husk below 800°C is amorphous, since the works of Kapur [98]. It does seem that particles of silica in rice husk ash are agglomerates of small nano range particles. Thus, it is very common to find aggregates of silica fines forming globules or platelets of varied sizes as seen in Figure 2.6. The first report of production of silica from rice husk was made by Conradt [56] and Liou [61] followed to use the same term later in his work and since then, other researchers [120] have always stressed the term in reporting their works. From the investigations in our laboratory, we have found that not much work or processing is required to obtain nano silica, since the natural form in which it resides in the husk is a wide distribution of sizes in the nano range, which is less than 100 nm.

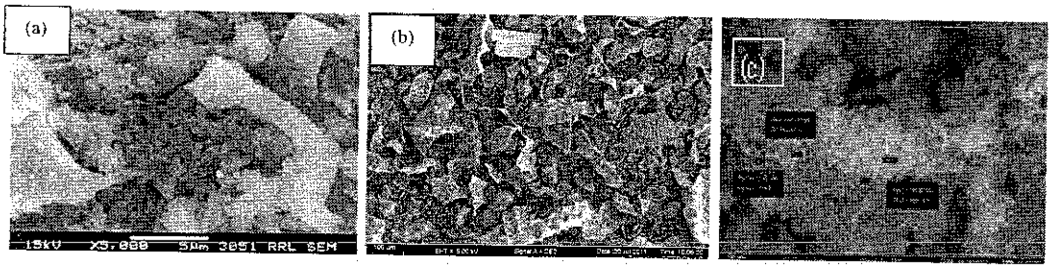


Figure 2.6: Morphology of Rice husk silica (a) SEM micrographs showing mixed platelets and globules [82]; FESEM micrographs revealing platelets and (c) agglomerated nanoparticles [from our laboratory]

Also studied is the chemical species that exist within the silica produced from rice husk. To demonstrate that the available chemical species in rice husk silica is process dependent, Hamdan *et al.* [90] and Mochidzuki *et al.* [93] reported similar data on the species available in rice husk silica, using ^{29}Si Nuclear Magnetic Resonance (NMR), when they produced rice husk silica via the hydrothermal process. The ^{29}Si MAS NMR spectra of rice husk silica presented in Figure 2.7 clearly show the variation of the chemical species with processing temperature.

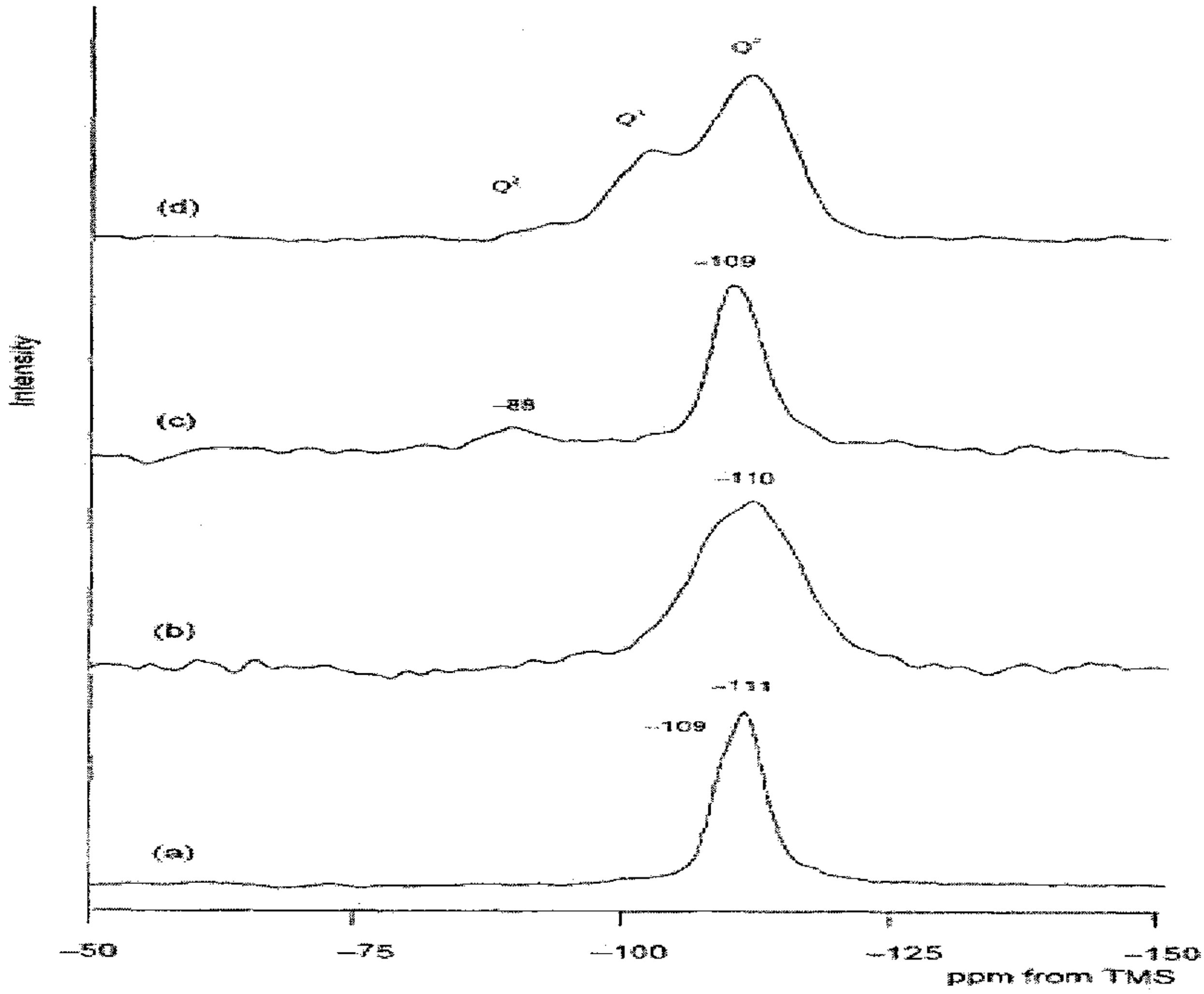


Figure 2.7: ^{29}Si MAS NMR spectra (a) open field burned (b) and (c) are muffle furnace processed at 700 and 1000^{0}C respectively, (d) hydrothermally processed samples [90]

A detailed examination of the spectra reveals important features. As explained by Hamdan *et al.* [90], the spectrum of sample Figure 2.7(a) consists of a single intense and narrow peak at - 111 ppm, which corresponds to the presence of Q4 line of siloxane bonds of the crystalline trydimite and a shoulder at - 109 ppm corresponding to β-cristobalite [90]. This observation is also true for sample Figure 2.7(c), and is expected, since the processing routes involved exposure of the rice husk to temperatures in excess of 700°C. The ^{29}Si MAS NMR spectrum of sample Figure 2.7(d) consists of peaks with chemical shifts of around δ= 90, =100, and =110 ppm, which correspond to the presence of Q2, Q3, and Q4 units, respectively, that is, silanediol units [$(OH)_2{*}Si(OSi)_2$], silanol units [$(OH){*}Si(OSi)_3$], and silicon-oxygen tetrahedral frameworks [$*Si(OSi)_4$], respectively.

Mochidzuki *et al.* [93] did a more detailed study of the species change with temperature and explained that the original rice husk silica consisted of 8.9% Q2, 60.3% Q3, and 30.8% Q4 units and that the percentage of Q4 units existing in the samples tended to increase with increasing treatment temperature, though Q2 and Q3 units remained at non-negligible percentages, since the maximum temperature he worked was 243°C. Going by the work of Hamdan *et al.* [90], there is a complete absence of Q2 and Q3 units, with the Q4 bandwidth increasing when we examine the spectrum for sample Figure 2.7(b). This suggests that the silicates with Q2 and Q3 structures were converted to Q4 silicates by the thermal treatment and since traces of Q2 and Q3 units existed in samples Figures 2.7 (a, c and d), the temperature around 700°C is optimal for the production of high purity silica devoid of silane-diol and silanol units.

2.4.6.4 Whiteness

One important property worthy of mention is the whiteness or more appropriately, colour of the silica produced at the end of each process. When working with an open field pile burning of fresh rice husk (Figure 2.3(a)), there are often points of incomplete combustion within the pile, resulting in points within the pile having particles of pyrolized husk as depicted in Figure 2.3(b) earlier presented. Once this happens, black coloration due to the un-burnt carbon remains within the product. Chandrasekhar *et al.* [87, 105] have done extensive studies on the optical properties of rice husk silica processed using different acid pre-treatment methods, and concluded that in processes where there has been substantial leaching of the alkali metal oxides especially the oxide of potassium, brightness and whiteness increase. They attributed this trend to the fact that when the husk is not substantially treated, the alkali oxides enhance the surface melting of silica, thereby entrapping carbon within the silica; the more the entrapped carbon, which is sometimes referred to as residual carbon, the darker the colour of the husk.

2.4.7 Guide to Rice Husk Silica Production Process Selection for Specific Application

The impurities contained in rice Husk silica could have implications in some of the applications they are put to use; while in some others, they are beneficial. It is therefore important to know what characteristics are needed in an intended application which would therefore, affect the choice of the purification degree that would be necessary for such an application. Table 2.6 gives a summary of applications that rice husk silica could be used for. The level or purity required is also indicated and links researchers with each application.

Table 2.6: Different applications and purity levels required of rice husk silica

Application	Desirable qualities	References	Purity Level	Recommended process
Fillers in polymers	Ability to retard thermo-oxidative and photo degradations. Possession of some silanol group to enhance coupling and good level of residual carbon to inhibit photo degradation	[123-131]	Pure, but possessing Q2 and Q3 groups	Hydrothermal process
Cement and Concrete	High reactivity. High surface area, absence of crystallinity	[16, 54, 66, 76, 132]	Ranges between 95-98% and possessing Q2 and Q3 groups	Acid pre-treatment before incineration at temperatures less than 700^{0}C
Zeolites	High purity and high porosity	[133-136]	Ranges between 95-98% silica	Acid pre-treatment before incineration at temperatures less than 700^{0}C in regulated environment
Aerogels	High purity	[81, 82]	> 99.5% silica	Acid pre-treatment before incineration at temperatures less than 700^{0}C in regulated environment
Cordierite	High purity/ reactivity	[87, 137]	> 99.5% silica	
SiC	Complex	[83, 84, 138]	> 99.5% silica	Complex

2.5 Manufacturing Process of Silica Refractory

It is important to review the processes involved in the manufacture of silica refractory bricks in order to establish a manufacturing route for the production of silica bricks from rice husk. Of course, discussion of these processes is replete in literature [2, 3, 7]. These literatures agree on the processes used for silica brick manufacture, which include extraction, crushing, grading, compounding, moulding and firing in the presented sequence. These processes are now briefly reviewed.

2.5.1 Extraction

The starting raw material for the production of silica refractory bricks is quartz, obtainable from sand, quartzite, ganister, or flint [2]. The raw material is extracted from its deposit in the earth and is cleaned of other foreign or extraneous materials. It is then passed on to the next stage, which is crushing.

2.5.2 Crushing

The crushing stage involves some sub-processes, carried out on the extracted raw material, either by using jaw crushers, ball mills or rod crusher [2, 3]. The crusher choice is dependent on the particle size intended to be obtained from and used in the moulding process. When ball milling is used, the particle size is assumed fine enough, so the grading process is often by-passed. Otherwise, from the crushing process, the grading process follows.

2.5.3 Grading

Particle size distribution affects the mechanical integrity of the bricks and therefore, it is necessary to grade the crushed material to ensure that the bricks produced are composed of a particular particle size range. Screening is accomplished by using magnetic separation or through the use of meshes, as suggested by Chesti [2]. On completion of the grading exercise the compounding process commences, which is discussed below. This refers to mixing the constituent elements that make up the brick in the appropriate proportions. This process is vividly explained by Chesti [2] as described next.

2.5.4 Compounding

The compounding is done by adding 1-2% milk of lime or hydrated lime plus other bonding agents such as sulphite lye, to the graded silica. Moisture content of between 7-9% (if the moulding is to be carried out by hand) is added and the composition is mixed thoroughly. The milk of lime performs two functions, which are: to act as mineralizer for the early production of tridymite and cristobalite and also, to act as bonding agent, improving the cold crushing strength of the refractory. Other mineralizers that may be used include iron oxide, borax, oxides of magnesium and fluorides, phosphates and carbonates of sodium, potassium and lithium. However, some researchers [139] have warned against the use of oxides of iron as mineralizers, since they have the propensity to reduce refractoriness and decrease the corrosion resistance of the bricks, through the encouragement of the formation of the monoxide of silicon. The deleterious effects of the use of sodium-based mineralizers have already been reviewed in section 2.3. Due to the availability and low cost of calcium oxide, it still remains the most widely used of all mineralizers in the silica refractory bricks production [10, 140].

2.5.5 Moulding

Moulding is carried out in the mixed materials at a semi-dry state, accomplished by either hand- or machine- moulding. The amount of moisture content required in the mix differs, depending on what moulding method is used. For hand moulding, Chesti [2] has prescribed a moisture content of about 7-9%, which is higher than the moisture content used in machine moulding. The disadvantages of hand-moulded bricks may include uneven hardness density, but machine moulding may result in poor thermal shock resistance due to the fact that a highly compacted mass is liable to crack as a result of intergranular expansion.

2.5.6 Firing

The firing process is made up of two stages, which are drying and the burning [7]. The drying process involves laying out the bricks in a well-ventilated room, or sometimes they can be dried on hot floors to minimize period of drying to about 12 hours (Chesti [2]). Ordinary drying takes about 48 to 96 hours, in order to ensure that drying is carried out up to less than 0.2% level of moisture retained in the brick.

The drying process is followed by burning or firing, in which the bricks are laid in a batch-type kiln. They are fired slowly past the critical temperature range of between 400 and 600°C, right up to between 1450 and 1500°C. The bricks are then soaked at this temperature for between 10 and 20 hours [2, 3, 7]. This is to allow for the formation of tridymite and cristobalite, the grafting elements in the bricks, ensuring maximum strength.

Chesters [3] in explaining the function of lime in the silica brick manufacturing process, quoted the work of Dale [45] thus:

> *"above 800°C, interaction between the lime and the free quartz surfaces begin to interact, leading to the formation of lime-silica glass, and as the temperature rises towards the soaking temperature, the lime-silica glass becomes saturated, which can devitrify, precipitating tridymite. The soaking time is essential for a mature formation of the tridymite".*

It is expedient to evaluate the properties of the produced silica bricks in order to establish that they meet requirements necessary for refractory application. Thus, characterization procedures necessary in refractory practice are hereunder reviewed.

2.6 Characterization of Refractory

Refractory materials are made in varying combinations and shapes depending on their applications. According to Carniglia and Barna [26] general requirements of refractory materials are that they should:

- Withstand high temperatures

- Have the ability to conserve heat
- Withstand sudden changes of temperatures (having good spalling resistance)
- Withstand the action of molten metal slag, glass, hot gases, *etc*
- Withstand load at service conditions (having good mechanical properties).

It is important therefore to test developed refractories to ascertain their properties. Refractory properties are many and are either physical, mechanical, thermal or even chemical. While some of these properties relate to the design and handling of refractories, some others characterise the performance evaluation of the refractories. However, for a general characterization of refractory, Baxendale [141] presented a good categorization of refractory properties as shown in Fig 2.8, which shows some examples of available tests for refractories.

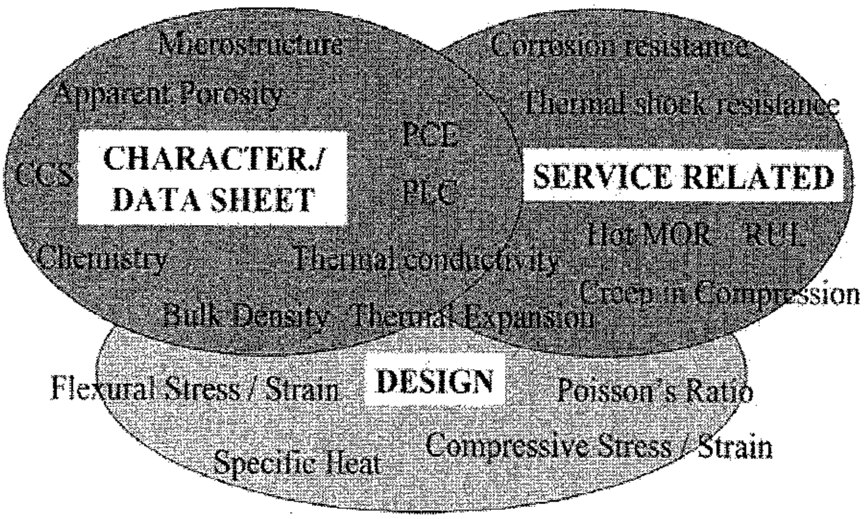


Figure 2.8: Categorization of refractory materials properties [141]

These tests generally fall into three functional areas, although, as we can see, some tests cut across more than one category. According to Baxendale [141], these functional areas into which these tests fall are: characterization/data sheet properties (these properties could also be termed physico-mechanical and include microstructure, bulk density, apparent porosity, modulus of rupture or its compressive strength at ambient temperature), service-related properties (such as pyrometric cone equivalent (P.C.E.), hot modulus of rupture (HMOR), refractoriness under load (R.U.L.) and permanent linear change (P.L.C.), and design data (such as compressive and flexural, stress–strain and abrasion behaviour). Some properties cut across either two or the three categories. For instance, thermal conductivity could be seen as a physico-mechanical property as well as it fits into the service related category. Thermal expansion is an example of refractory property which falls into the three categories.

To measure these properties, several standards (the BS, ISO, DIN or ASTM) have evolved. Each has its own prescriptions for each property to be evaluated, but with slight overall differences. In all, the ASTM standards seem to be more universal and hence are referred in this work.

2.6.1 Physico-mechanical properties

2.6.1.1 Bulk Density (BD) and Apparent Porosity (AP)

The bulk density of a porous material is defined as the ratio of mass of the material to its bulk volume, whereas the apparent porosity is the ratio of open pores to the bulk volume of the material [142]. The latter value is expressed as a percentage.

ASTM C20 [143] states clearly the procedures to be taken in measuring these properties. The determination of these properties is accomplished by boiling the specimens in water, with details expressly spelt out in that procedure (ASTM C20) [143]. In it,

$$Bulk\ Density = \frac{Dry\ weight}{Saturated\ \ weight - suspended\ mass} \times 1\ gcm^{-3} \qquad (2.1)$$

$$Apparent\ porosity = \frac{Saturated\ \ weight - dry\ weight}{Saturated\ \ weight - suspended\ mass} \times 100 \qquad (2.2)$$

2.6.1.2 Cold Crushing Test (CCT)

The cold crushing strength of a material is the maximum load at failure per unit of cross-sectional area when compressed at ambient temperature. It is calculated from the relation given in equation (2.3).

$$Failure\ stress = \frac{Load\ (in\ N)}{Area\ (in\ mm^2)} \tag{2.3}$$

This test procedure is fully described in ASTM C133 [144].

2.6.1.3 Modulus of Rupture (MOR)

Modulus of rupture is the maximum transverse breaking stress applied that a material can withstand before fracture [142]. The property gives an indication of the bond strength of the refractory, which results from its chemistry and mineralogy after production. The test method is either of two types- the three- or four-point arrangement.

The test piece is placed between supports a set distance apart and loaded to failure at the centre of the bar by a third loading arm. This is known as the three-point arrangement. This three-point arrangement is most commonly applied to refractory materials, although in some critical applications, though not standard practice [141], a four-point arrangement, where a greater volume of the test bar is placed under applied stress by two upper loading arms, is preferred. A four-point arrangement leads to lower overall failure stresses and gives an indication of the minimum failure stress of a material.

The calculations for modulus of rupture in three-point and four-point arrangements are made from ASTM C133 [144]:

$$Failure\ stress\ (3-point) = \frac{3Pl}{2bd^2} \tag{2.4}$$

$$Failure\ stress\ (4 - point) = \frac{3Pa}{2bd^2} \tag{2.5}$$

where

p = load in Newton or lbs

l = test span in mm or in.

b = specimen breadth in mm or in.

d = specimen depth in mm or in.

a = distance between lower and upper loading points in mm or in.

Units of failure stress are N/mm^2 (MPa) or lbs/in^2.

2.6.1.4 Pyrometric Cone Equivalent (PCE)

The pyrometric cone equivalent gives an indication of the refractoriness of a material, that is, its ability to withstand high temperatures in an unstressed situation. The ASTM code that regulates this test is ASTM C24 [145]. The method applies particularly to aluminosilicate materials. Determination of the P.C.E. can ensure that a refractory selected for a particular application is operating well below the onset of melting.

In the procedure, a standard refractory cone shape is prepared from the test material and heated together with a number of standard cones in an oxidizing atmosphere at a specified rate. The purpose of the test is to identify the point at which the tip of test cone bends over. Its behaviour is then compared to that of the standard cones. The most similar standard cone to the test cone gives a corresponding temperature rating. Sometimes the rating may be reported between two standard cone values if the softening point occurs between the two. Depending on availability, one of Orton, Seger, or ISO cone rated systems are used in this procedure.

2.6.1.5 Mineralogical Analysis

Often, it is necessary to carry out materials characterization in terms of chemistry, before they are batched for the refractory production process. In the same vein, phase identification can be useful in cases of identification of unknown materials or products. In some other cases, it may be necessary to confirm if certain phases have formed during a firing process or that components have not broken down or removed during service.

For materials chemistry determination, ASTM C416 [146] has prescribed the use of x-ray flourence (XRF) while X-ray diffraction (XRD) analysis provides a means by which different crystalline phases can be characterized and identified.

2.6.2 Service Related Properties

2.6.2.1 Modulus of Rupture at High Temperature (HMOR)

Modulus of rupture at room temperature was introduced earlier and, as indicated, is useful for quality assurance, but gives little indication of in-service performance, unlike the same test carried out at elevated temperature. According to Baxendale [141], the nominal specimen size used in national and international standards for dense and insulating refractories is again 150 mm x 25 mm x 25 mm or similar, and support test span is approximately 125 mm. Specimen temperature is measured by a thermocouple placed centrally underneath the test bar. The specimens are heated to the test temperature at specified rates. Following a dwell for a set period at the test temperature, the samples are loaded to failure at a designated stress rate. The stress rate differs for dense and insulating refractories.

2.6.2.2 Refractoriness Under Load

Refractoriness under load (RUL) is the ability of a material to withstand specific conditions of load, temperature, and time [147]. This is dependent on the softening point and the amount of glass or melt phase within the refractory system.

The specimen is placed in a furnace between refractory plates and in contact with a dilatometer system, which is in turn attached to an extensometer to measure deformation. A specified load is applied to the specimen, and the material is then heated to the maximum test temperature or until a particular percentage deformation is reached.

2.6.2.3 Thermal Shock Resistance

Thermal shock resistance is the ability to withstand rapid changes in temperature with minimal cracking [147]. This situation may occur under conditions when the material is heated or cooled suddenly such as with submerged entry nozzles, under thermal cycling such as in the regenerators of a glass furnace, or when subjected to a severe thermal gradient such as with sliding gate plates. Incompatible changes in dimensions at these times may lead to failure in regions where local strain exceeds the tensile failure strain.

Certain materials—for example, silica refractories—are more vulnerable to thermal shock if heated rapidly over temperatures where thermal expansion is high as a result of test changes. Test temperatures for silica can often differ from other refractory materials. Tests tend to take place at temperatures where expansion is high.

2.6.2.4 Permanent Linear/ Volumetric Change (PLC)

This is a measure of the permanent changes in dimension of a refractory, either in terms of expansion or contraction, after heating ideally to an anticipated hot face service temperature or material classification temperature. This should indicate the maximum expected dimensional change in a stress-free condition. Within the scope of the various test methods available, the change in dimensions is reported with corresponding test duration. Firing temperature and soak times at temperature may vary depending on the material and its operating conditions. Across the various methods available, the test piece size can be of a standard brick or rectangular prisms or cylinders. This implies that shape or size is of no critical importance.

Dimensions are measured at identified points on the test piece. The specimens are then fired in accordance with a specific heating schedule in an oxidizing atmosphere for the set duration. Minimum firing temperatures start around 800^0C, and for dense refractories test duration is nominally five hours [148]. The dimensions are re-measured following firing at the same identified points following firing, and the percentage change is calculated.

For linear changes, the result is expressed as follows:

$$\delta L = \frac{L_i - L_f}{L_i} \times 100 \qquad (2.6)$$

where

L_i = initial length

L_f = final length

Gilchrist [7] has said that mechanical strength and general behaviour of silica refractory at any point in time depends to a large extent on the phases that are present at that material state and time. Therefore, properties of refractories are time and service dependent. One important step in refractory development is to be able to produce refractory that could easily be handled for installation and other purposes. This is governed by the physico-mechanical properties of the refractory. The physico-mechanical properties are themselves derivatives of the minerology of or phase formed in the refractory body after firing. For this reason and for the fact that this work has as its core, the development and establishment of the optimal manufacturing process parameters for rice husk silica refractory production, attention shall be focused on the following tests: microstructure, bulk density, apparent porosity, modulus of rupture at ambient temperature, pyrometric cone equivalent (P.C.E.) and permanent linear change (P.L.C.).

2.7 Why Rice Husk?

The outermost layer of the paddy grain is the rice husk, also called rice hull. It is separated from the brown rice in rice milling. Rice husk is one of the most abundant agricultural wastes on many sub- urban and rural settlements around the world, where rice farming thrives.

Around 20% of the paddy weight is husk or hull [71] and this contains approximately 20% opaline silica in combination with a large amount of the phenyl propanoid structural polymer called lignin [72]. Burning rice husk produces *rice husk ash* (RHA) and if the burning process is incomplete *pyrolized rice husk* (CRH) is produced. According to a report by Bronzeoak Ltd [149], rice husk is unusually high in ash compared to other biomass fuels – approximately 20%. The report went further to state that the ash contains about 92 to 95% opaline silica. In nature, silica (SiO_2) occurs as seven distinct polymorphs: quartz, cristobalite, tridymite, coesite, stishovite, lechatelerite (silica glass), and opal; the latter two are amorphous, [41, 150]. Also, significant early contributions were made by Florke [42], who hypothesized on the basis of XRD that opals are disordered intergrowths of cristobalite and tridymite and by Jones *et al.* [43], who determined that gem-quality opals are 3-dimensional arrays of amorphous silica spheres. Generally, opal has been described as a hydrated silica polymorph ($SiO_2.nH_2O$), highly porous and lightweight, with a very high external surface area (report of Bronzeoak Ltd, [149]).

Such a high percentage of silica as contained in rice husk is very unusual within nature [71], and this intimate blend of silica and lignin makes the rice husk not only resistant to water penetration and fungal decomposition, but also resistant to the best efforts of man to dispose of it and since the husk represents on average about 20% of the rough harvested weight of rice (paddy), our planet ends up with an abundance of this scaly residue.

For instance, in 2010 world paddy production was over 700 million tons [70]. Consequently, over 154 million tons of rice husk were generated in 2010. While there are some uses for rice husk, it is still often considered a waste product in the rice mill and therefore, often either burned in the open or dumped on wasteland [151].

There is also a striking statement made by Olivier [72], which reads:

> *"The chemical structure of the rice hull, containing amorphous silica bound to water, closely resembles that of the opal, and this gives the rice hull some fairly amazing properties. Nowhere could we ever find a cereal by-product so low in protein and available carbohydrates, and yet, at the same time, so high in crude fiber, crude ash and silica".*

Juliano [74] has also opined that of all cereal by-products, the rice hull has the lowest percentage of total digestible nutrients (less than10%). These statements corroborate the fact that rice husk is truly a waste.

The above discourse explains why rice husk is chosen to be used in this work as the source of silica- an attempt to turn waste to wealth. This will have some benefits as discussed in the section on importance of this research (section 1.5).

2.8 Chapter Summary

The chapter has discussed classes of refractories and followed with a brief survey on silica refractory research and development. The brief survey has shown that the research gaps in silica refractory research and development have not been resolved or filled by current research. The review also identified a new, renewable source of silica for refractory production- rice husk silica.

Having identified rice husk as a possible source of silica for refractory manufacture, a review of the processing methods of rice husk silica and the developed properties was done. It is clear from the processing methods reviewed, that apart from TORBED system for the production of silica of purity around 95% which has been commercialized, all other processes still have the problem of scalability from laboratory scale to industrial levels, calling for research into a viable processing technique.

The chapter ended with a review of the characterization methods of refractories and adduced reasons for focusing the tests carried out in this research on the characteristic data properties, rather than service related properties. The specific methods employed to accomplish all the investigations carried out in the research are presented in chapter 3.

CHAPTER 3

METHODOLOGY

3.1 Chapter Overview

This chapter discusses the experimental procedures used in conducting the various tests undertaken in this research. The chapter begins with an overview of the entire processes of the research presented in a chart format (Figure. 3.1). From the Figure.3.1, it is evident that the entire research is divided into two phases or parts: the first part deals with the production, characterization and manufacturing process optimization of rice husk silica (RHS); while the second part treats the production, characterization and manufacturing process optimization of RHS refractory. Thus, the chapter is discussed in line with these two major splits, presented in detailed specific steps undertaken to accomplish each test, organized part by part.

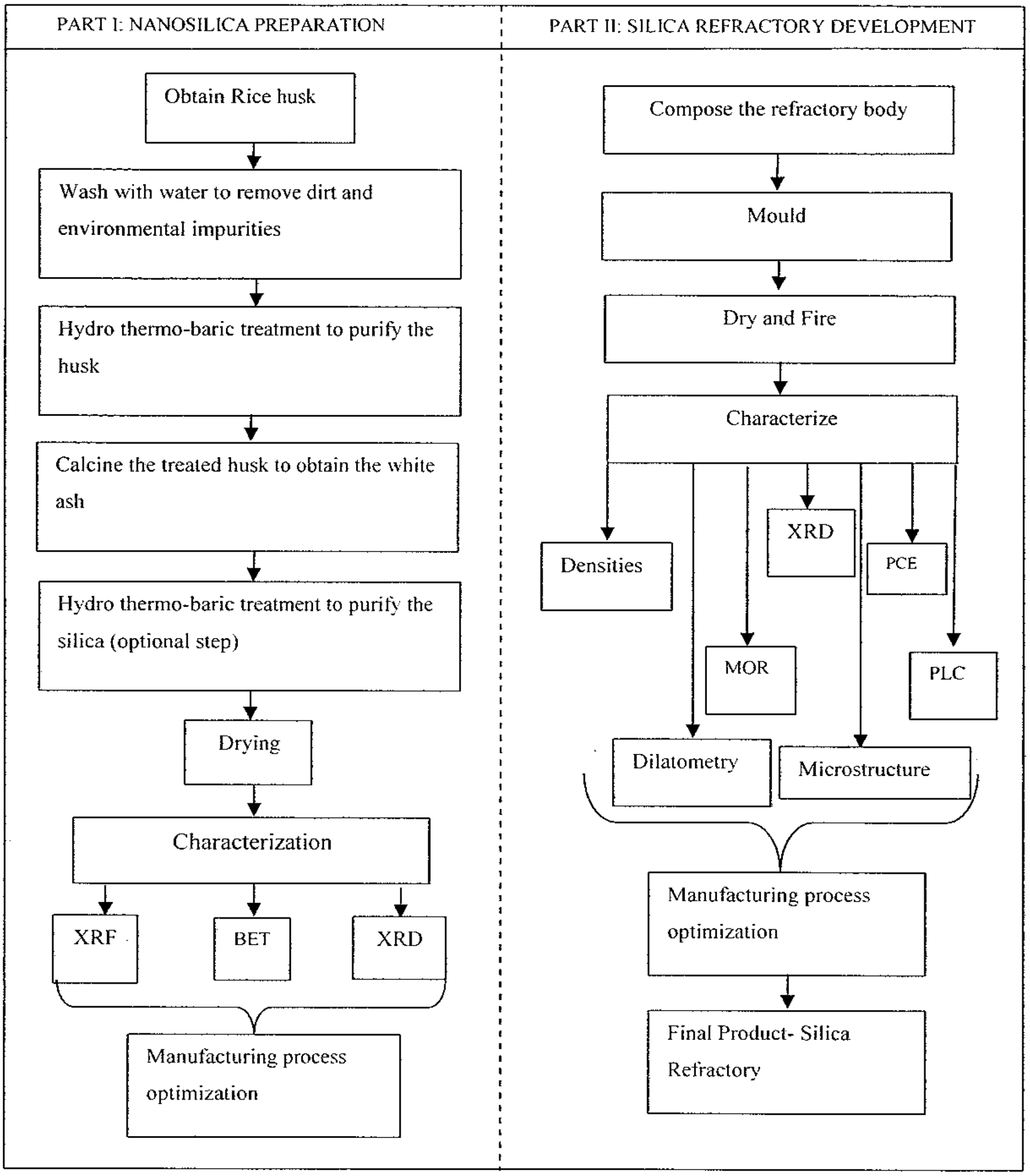


Figure 3.1: Overview of the entire research

3.2 Production and Characterization of Silica from Rice Husk

The work carried out under this part of the research is condensed into the processes depicted in Fig. 3.2.

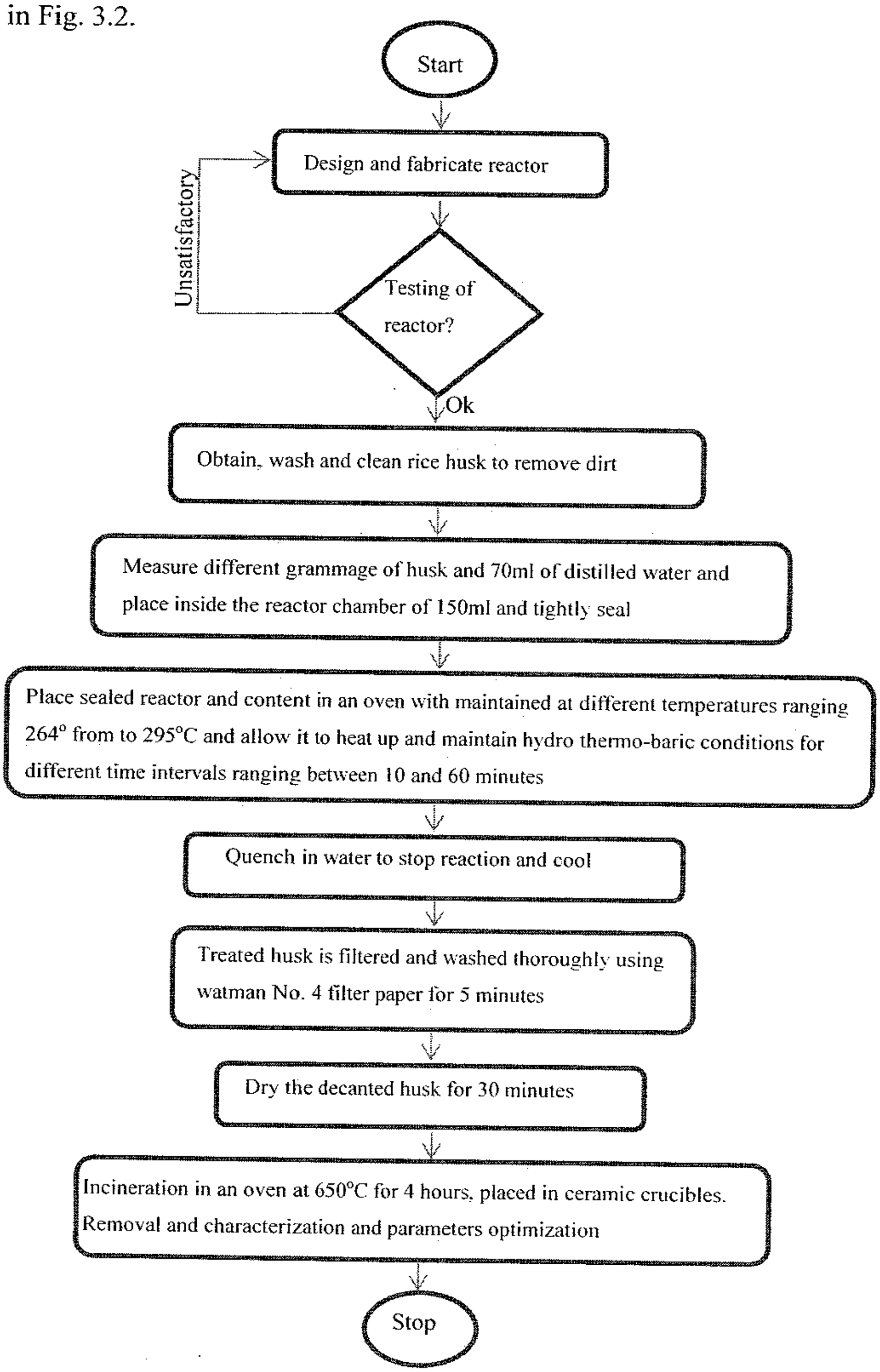
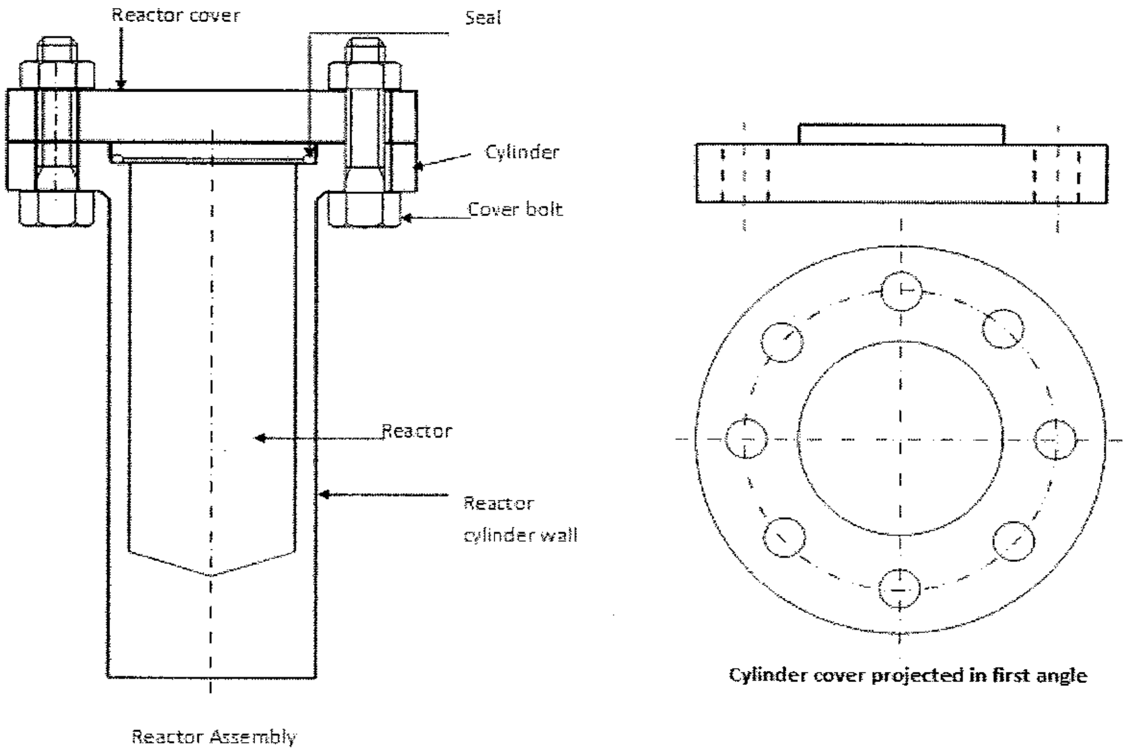


Figure 3.2: Stages and process involved in silica production from rice husk

The steps/ methods used at each stage in the production of RHS would now be discussed.

3.2.1 The Hydro Thermo-baric Process: Principles and Design



Reactor Assembly

Cylinder cover projected in first angle

Figure 3.3: The synthesized reactor

3.2.1.1 Reactor Parts Design: the Cylinder Thickness

In the choice of material used for this design steel readily comes to mind because of its mechanical properties. Stainless steel 304 was used in the design, with yield strength (tensile) as 215MPa, with a factor of safety of 5, and cylinder internal diameter, d_1 of 20 mm. The maximum operating temperature selected for this reactor was 300^0C, in order to avoid stainless steel sensitization. At this temperature, steam has saturation pressure of 8.59MPa [152]. The task was to determine r_2 and then the thickness, $t= r_2-r_1$, of the reactor cylinder wall that would be able to withstand these operating conditions of temperature and pressure.

For the purpose of safety, the cylinder is considered as a thick one and the formula for calculating thickness of such a cylinder with internal and external radii of r_1 and r_2 respectively subjected to internal pressure, S_1, for a material with allowable stress S_a, is given by the Lame's equation [153]:

$$S_a = S_1 \frac{(r_2^2 + r_1^2)}{(r_2^2 - r_1^2)} \tag{3.1}$$

3.2.1.2 Cylinder Cover Design

The thickness, t_1 of a plate with a diameter, d, supported at the circumference and subjected to an operating pressure, S_1, which is uniformly distributed over the area described by d, is given by the formula [154] :

$$t_1 = k_1 d \sqrt{\frac{S_1}{S_a}} \tag{3.2}$$

where Sa and S_1, are as previously defined; k_1 is a material factor and is dependent on clamping conditions and for our condition of round bolting, it is given as 0.35 [154]. For design safety, any thickness not less than the thickness of the cylinder cover as designed using the above formula would do.

3.2.1.3 Cylinder Cover Clamping Bolt Diameter Specification

For the design of a bolt, the following formula suffices:

$$F_b = F_2 + \frac{k_b}{k_b + k_c} F \tag{3.3}$$

Where k_b and k_c are respectively stiffness of the bolt and the reactor cylinder cover/flange materials. In this case, both materials are same, that is, $k_b = k_c$

So that,

$$F_b = F_2 + \frac{1}{2} F$$

Which implies that for the 8 bolts,

$$F_b = F_2 + \frac{F/8}{2} \tag{3.4}$$

Therefore stress on each bolt is:

$$\sigma_1 = \frac{F_b}{A_t} \tag{3.5}$$

F_2 is the pre-tension applied on the bolt.

3.2.1.4 Heat Transferred Through the Material to Heat up the Reactor and Content

There is need to determine how long it takes for the reactor heat up to the working temperature of 300°C. This is calculated from the relation:

$$\text{Time to heat up, T} = \frac{Quantity\ of\ heat\ required\ to\ heat\ reactor\ and\ content\ to\ 300°C}{Rate\ of\ heat\ transferred\ to\ reactor\ and\ content\ per\ second}$$

Quantity of heat required to heat up reactor and content to 300°C (not considering convection effects) is approximately

$$Q = m_r c_r \Delta T + m_w c_w \Delta T \tag{3.6}$$

In this design, mass of reactor, m_r was determined to be 3.14kg; specific heat capacity of reactor material (stainless steel grade 304), c_r = 500J/kg°C; mass of water, m_w anticipated to be used is 0.15kg; while specific heat capacity of water, c_w = 4200J/kg°C.

3.3 Materials and Methods for the Hydro Thermo-baric Purification Process

3.3.1 Materials

Rice Husk: This was obtained from the stockpiled bags of rice husk purchased by the Universiti Teknologi PETRONAS for the Civil Engineering department, for experiments involving the determination of the pozzolanic effects of rice husk ash. The husks were washed thoroughly with water, rinsed and sun-dried. They were again dried in oven until constant moisture content of 7% was attained. The dried husk coded DRH were collected and stored in dry air-tight plastic containers, for use in other procedures.

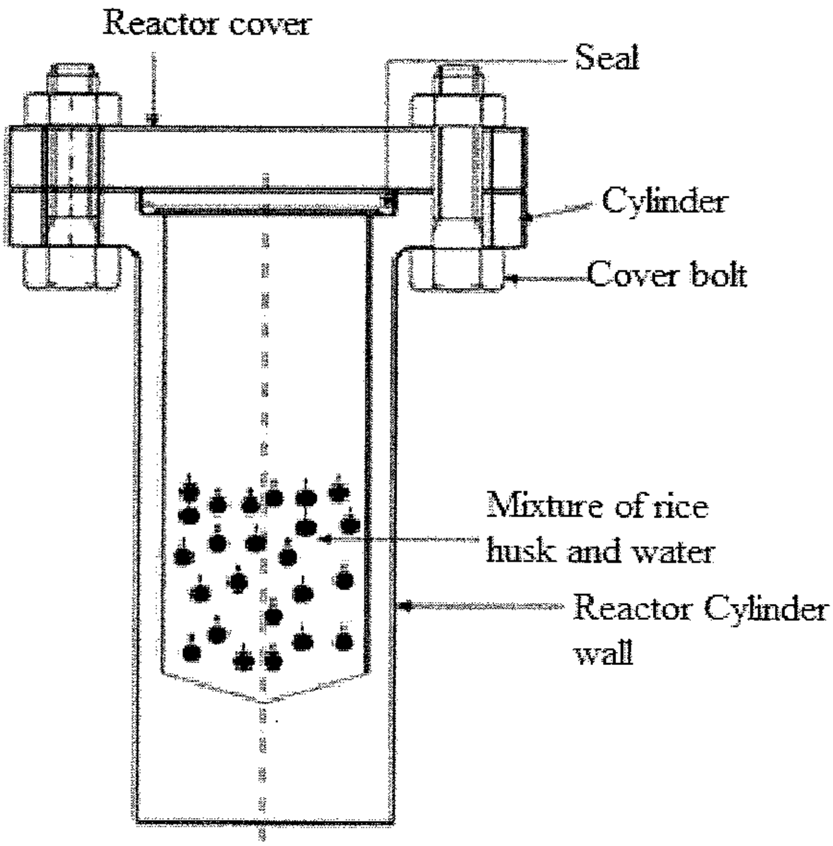
3.3.2 Methods

3.3.2.1 Hydro Thermo-baric Treatment of Rice Husk

The setup used for this experiment is shown in Figure 3.4. The reactor vessel designed as discussed earlier consisted of a 150ml cavity, in which the purification reactions took place. In this process, a certain amount (Table 3.1) of the DRH sample was placed in the reactor cavity, with the vessel filled with 70ml distilled water. The reactor vessel as well as content was sealed tightly and heated up in an oven until it reached a predetermined temperature called the soaking temperature (Table 3.1). The soaking was done at each of these temperatures for varied periods called soaking time (Table 3.1) to maintain hydro thermo-baric conditions within the reactor. The temperature, soaking time and the quantity of husk used in the investigations depended on the experimental conditions as explained in the optimization procedures in sub-section 3.3.2.3. At the end of each soaking period, the reactor vessel was removed from the oven and submerged in cold (room-temperature) water to cool it and to stop the reaction within it.

The mixture of the solvent and solute in the reactor was separated into filtrate and residue by watman number 4 fibre glass filter paper. The residue was dried and kept in airtight plastic containers for further processing and investigations.

As a control specimen, 5g of untreated rice husk was pyrolized in an oven at 300°C for 30 minutes.



Reactor Assembly
Figure 3.4: Setup for the hydro thermo-baric process

3.3.2.2 Obtaining the Silica (Incineration Procedure)

After the hydro thermo-baric treatment, all samples (including the pyrolized control sample) were placed in separate zirconia crucibles inside a box furnace with static air and the temperature raised by 10°C per minute until 650°C and they were soaked at this temperature for four hours, in order to remove any remnants of cellulosic materials remaining in the residue. After the incineration procedure, the agglomerates obtained was pulverized manually in a ceramic mortar for 10 minutes each and thereafter submitted to property characterization studies.

3.3.2.3 Process Optimization

It was necessary to obtain optimal conditions for the hydro thermo-baric process factors. Three factors were identified: soaking temperature, soaking time and rice husk quantity (g) to water (70ml) ratio. The reasons for selecting these factors for investigation are not farfetched. First, chemical reactions can only occur if and only if the right chemical species are present. In the theory of the HTB process given in section 2.4.5, it was stated that water auto-ionizes and or dissociates to form the hydronium and hydroxyl ions. These two chemical species caused the purification reactions to occur. Formation of both species is aided by high pressure. Water pressure increases with temperature and so temperature was selected as a factor. On the other hand, temperature is one factor which affects the rate of chemical reactions. Secondly, chemical reactions are dependent on concentration of the reactants and products. Since the impurities to be dissolved are in the husk and it is water that causes the reacting species to be present, there must be a certain ratio between the husk and water to favour these reactions to occur. Therefore, water to husk ratio became another factor that was selected for investigation. It takes time for reactants to proceed to form products, hence the need to vary the heating time. This was why soaking time was selected for investigation as well.

It is possible to use the factorial design of experiment, when all process factors are known and an expected output (response) is fixed to measure the effects of the factors on the process performance [155]. To use the factorial method, lower and upper limits of the factors are fixed and used for the design of mix. In order to determine the lower and upper limits of the process factors, preliminary tests using the one variable at a time (OVAT) method of experimentation, was carried out, as described explicitly in Table 3.1.

Table 3.1: Detailed design of experiment for HTB process factors optimization

Process factors	Investigation Type	No. of replications	Variable Levels
Water to husk ratio	HTB	3	1, 3, 5, 7, 9g of rice husk to constant Water volume (70mL)
	XRF	3	
Soaking temperature	HTB	3	251, 264, 276, 286 and 295^{0}C
	XRF	3	
Soaking time	HTB	3	10, 15, 30, 45 and 60 minutes
	XRF	3	

In employing the OVAT method, the hydro thermo-baric treatment was carried out as explained in the procedure described in sub-section 3.3.2.1. The treated rice husk was submitted to the procedure described in sub-section 3.3.2.2 to obtain white agglomerates from the husk. The agglomerate so obtained was subjected to XRF analysis to determine chemical composition, in a procedure described in sub-section 3.3.3.1.

As stated earlier, the purpose of the OVAT method was to determine the effect of each of these process factors on the purity (which is the main consideration in this work) of the RHS obtained from the HTB process. Around the region where each of the factors shows the best influence on the improvement on purity of RHS, a boundary was defined. The beginning of the boundary was termed the minimum level while the end of the boundary was termed the maximum level. These two levels of each factor are the levels required in the factorial process. The results of the OVAT method (discussed in section 4.2.3.1) favoured the choice of the factors levels shown in Table 3.2.

Table 3.2: Factors and levels employed in the factorial planning used in the optimization process

Variable name	Level	
	Minimum	Maximum
Water to Husk ratio (WTHR)	5	7
Soaking temperature (TEMP)	276	295
Soaking time (SOKT)	15	45

This gives a 2^3 factorial, having eight (2^3- 2-level to the power of 3 factors) runs. After each run has been submitted to hydro thermo-baric treatment and incineration procedures as described in sections 3.3.2.1 and 3.3.2.2 respectively, the percentage purity of the agglomerates, which is the response of the process to the changes in the variable levels, was determined using X-ray fluorescence (XRF) as described in section 3.3.3.1.

After obtaining the percentage purity for all the experimental runs, the data obtained were analyzed statistically using version 6 of design of experiment software called Design Expert®. The software used for the analysis uses a second degree polynomial, approximated by equation (3.7) (which is the usual statistics regression analysis approach), to predict the response, Y. This equation includes all factors as well as the most effectual way the factors interact in the observed process (in this case, the HTB process). The prediction equation is given as [155]:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \tag{3.7}$$

3.3.2.4 Testing the Effectiveness of Purifying RHS Using the HTB Process

It was necessary to establish the effectiveness of the hydro thermo-baric process in purifying rice husk silica. This was investigated by using the optimal conditions obtained from the optimization process described in the previous section. The purity of the RHS produced using optimum WTHR, TEMP and SOKT was analyzed using

XRF, as described in section 3.3.3.1. The result was compared with the purity level of the untreated rice husk ash.

3.3.2.5 Investigating the Process Factors Effect on the Product (RHS)

Literature has shown (see section 2.4.6.1) that transformation of RHS from its natural amorphous state to the crystalline state takes place at the threshold temperature of 700°C. The maximum temperature used in the HTB process is 300°C. Therefore, it is conclusive that the orignal state of the produced RHS would not be affected by the optimal temperature obtained from the optimization process (see section 4.2.9.2). Similarly, as shown in section 4.2.5, the effects of the factor- water to husk ratio- are very clear; it only affects the purity of RHS.

Consequently, it is only the factor- soaking time- that may affect the quality of the produced RHS. This is because at the the temperature range shown in Table 3.1, the lignocellulosic content of the rice husk would have pyrolized, generating carbon in the form of smoke. For this reason therefore, the factor investigated is varied soaking time, in order to determine the amount of the adsorbed carbon on the surface of the RHS. Adsorbed carbon can affect the reactivity of the RHS, hence the need to determine it.

From the foregoing therefore, investigations were limited to the effect of soaking time on the morphology, surface area and pore characteristics of the RHS. Confirmatory tests were done to demonstrate that the structure of the silica remained amorphous. For this purpose, XRD analysis was done for the untreated samples and the treated samples. The XRD analysis description is in section 3.3.3.2.

The Morphology was studied using FESEM and EDX as described in section 3.3.3.2. In the EDX investigation, the soaking times compared with the untreated RHS (coded UTD00) are: 15, 30, 45 and 60 minutes.

The surface and pore characteristics were determined by the BET method as described in section 3.3.3.3. Soaking time used were 10 and 30 minutes (coded HTB10 and HTB30 respectively) compared with the untreated sample (UTD00).

3.3.3 Product (RHS) Characterization

3.3.3.1 Chemical Composition

The ball-milled samples were subjected to chemical compositional analysis using X-ray fluorescence (XRF) (Bruker S4 Pioneer), to determine how much of the impurities in the RH have been eliminated, using the control sample results as bench-mark.

3.3.3.2 Physical Properties

Morphology was imaged with Zeiss Supra 55VP Variable Pressure Field Emission Scanning Electron Microscope (VP- FESEM), which also revealed the particle sizes of the samples. The same machine was used to carry out electron dispersive x-ray spectroscopy (EDX), to investigate the elemental balance of the silica. X-ray diffractometer (XRD) (Bruker D8 Advance) was used to determine the crystalline structure of the product. Each specimen was scanned in a range of $5° \leq 2\theta \leq 70°$ at a scanning speed of 4°/min.

3.3.3.3 Measurement of Surface Area and Pore Structure

Surface area, pore volume, and pore diameter of the samples were measured by a Micrometric analyzer (model: ASAP 2010) using nitrogen adsorption. The analyser uses the Brunauer–Emmett–Teller (BET) method to determine specific surface area. Single point total pore volume was calculated from the volume of adsorbed nitrogen at a relative pressure (P/Po) of approximately 0.984. Pore size distribution was obtained from the desorption branch of the isotherm using the Barrett–Joiner–Halenda (BJH) method.

3.3.3.4 Particle Size Analysis

RHS obtained from the hydro thermo-baric process was analyzed using a zetasizer, Nano ZS (ZEN 3600). Two grams (2g) of the RHS particles were homogeneously mixed with deionized water to make a dilute solution for the measurement of nanoparticles size. Homogeneous mixing was achieved through a combination of manual or mechanical and magnetic stirring. Several readings were taken, all at room temperature to establish consistency.

3.3.3.5 Process Yield

To evaluate the yield of silica from the process, a direct comparison was made between treated and untreated samples. DRH obtained from procedure described in section 3.3.2.1 were used for this evaluation. 5g of DRH was treated following the procedures described in section 3.3.2.1 and the treated husks were incinerated alongside 5g of untreated DRH, as described in section 3.3.2.2. The obtained agglomerates were weighed for both the treated and untreated rice husks, using analytical balance (Ohaus), with accuracy of 0.001g. Five replications (batches) were carried out.

3.3.3.6 Comparative Analysis of the HTB Process and other Available RHS Production Methods

In the choice of processing methods considered in the analysis, it was decided to exclude from the analysis processes which do not focus on product purity and structure improvement. Thus, open field burning and fluidized bed combustion of rice husk processes do not form part of comparison carried out. Basically, the processing methods considered were those which employed acid (mineral or organic), alkali or distilled water for treatment of the husk, either before or after (or combined mode-before and after) incineration. Direct comparison of quantitative results was made. Where possible, as in the case of structure and morphology, qualitative statements were considered. Detailed discussion of the information arising from the comparison made has been presented in section 4.2.9.

3.4 Production and Characterization of Rice Husk Silica Refractory

The goal of this part of the research was to apply the RHS derived from part 1 of the work to produce RHS refractory. It deals with the optimization of the factors affecting the manufacturing process and then concludes with characterization of the products manufactured. Shown in Figure 3.5 is the flow of processes involved in this part of the research. However, unlike the case of the optimization of the HTB process which employed a combination of both the OVAT and factorial optimization methods, the optimization carried out in this part of the research employs the OVAT method only. The consideration that informed this decision was that the OVAT method yielded optimal value for each of the factors chosen. These factors are: percentage mineralizer (Table 3.4); compaction pressure (see section 3.4.2.2) and firing temperature (Table 3.5).

The choice of these factors is based on information from literature. For instance, the presence of mineralizer affects the temperature of phase transformations which occur and the range of temperature over which the formed phases are stable. Also, compaction pressure affects the bulk density of the formed refractory. All of these activities affect the mechanical behavior of the manufactured refractory.

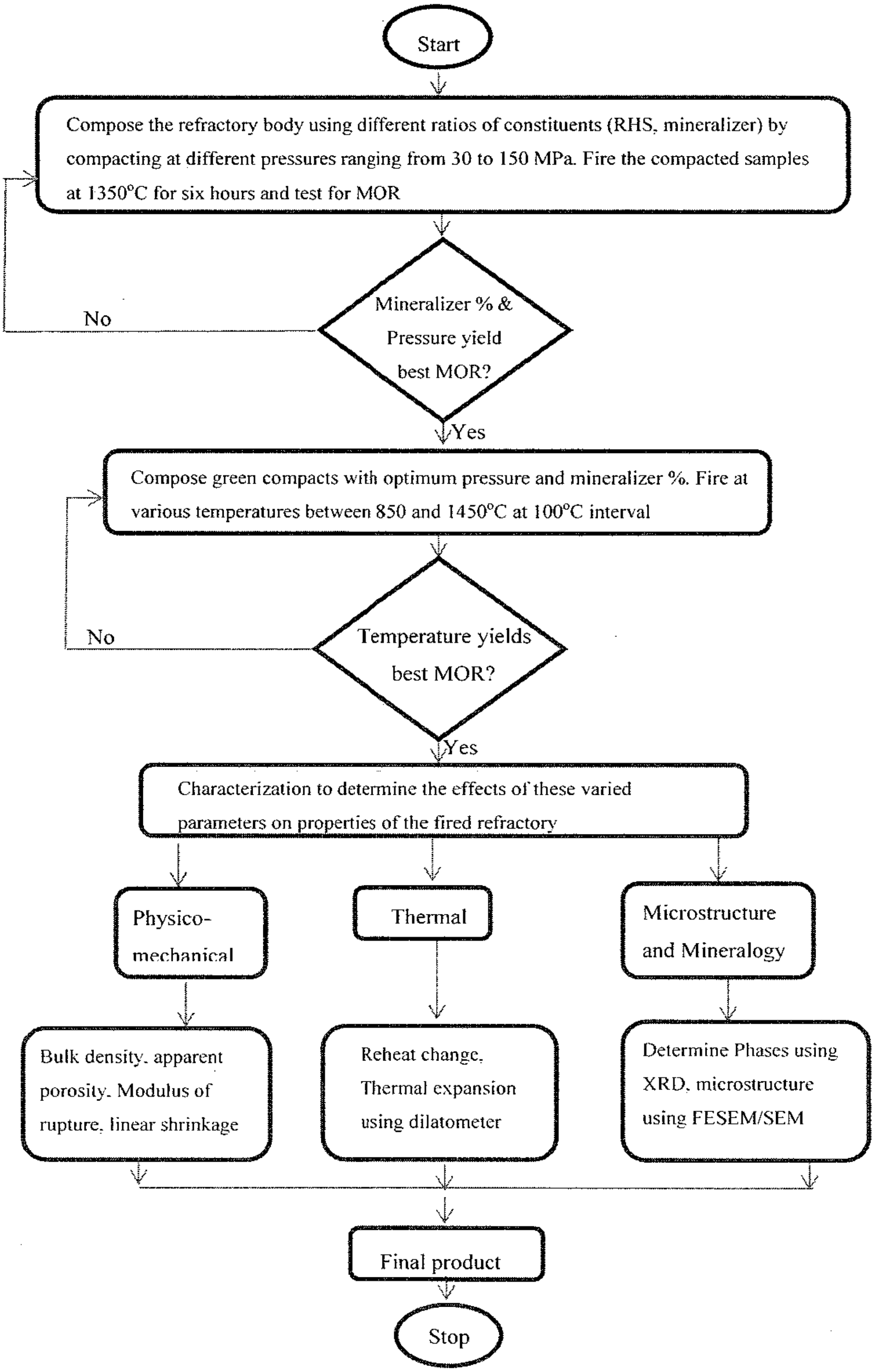


Figure 3.5: Overview of silica refractory production from rice husk and their characterization

3.4.1 Materials

RHS with adequate purity that met ASTM C416 classification standards [146] was obtained from Malaysian rice husk through the hydro thermo-baric process. The mean composition of the RHS determined by XRF is shown in Table 3.3 with average particle size of 117 nm as analyzed by Zetasizer (the distribution is shown in Figure 4.1). Analytical grade slaked lime ($Ca(OH)_2$), (R&H chemicals) with average particle size of 50 μm was used as mineralizer in compounding the refractory and pellets of Polyethelene glycol 8000 (PEG) (Merck) were as supplied. A solution of 5 weight percent concentration prepared from the pellets of PEG using standard measure of distilled water was used as the binder.

Table 3.3: Chemical composition of hydro thermo-baric treated RHS used in the investigation

Compound	Percent
SiO_2	99.04
K_2O	0.111
P_2O_5	0.376
CaO	0.180
Al_2O_3	0.210
Fe_2O_3	0.083

3.4.2 Methods

3.4.2.1 Optimum Ratio of Mineralizer to RHS Determination

For the experiments to determine the optimal value of the mineralizer needed for the refractory manufacture, composition was made as shown in Table 3.4. All weights were measured using analytical balance (Mettler Toledo) with an accuracy of 0.001g. An appropriate amount of the prepared PEG solution was added carefully to the powder mixes, to form slurry. The slurry was stirred for 1 hour to ensure homogeneous mixing of the powders and binder using a magnetic stirrer. The excess water was evaporated from the slurry in an oven at a temperature of 105 °C and the dry powder mix was pulverized in ceramic mortar to produce fines, with minimal agglomeration.

Calculated amounts of the homogeneously mixed powders were measured into mould and compacted under an arbitrary (though with recourse to art) chosen pressure of 105 MPa using an auto palletizing machine, to form refractory green bars of (35 x 9 x 6) mm^3, which were later fired at the temperatures stated in Table 3.5. To obtain the optimal ratio, the fired bars were tested for modulus of rupture (MOR). The choice of MOR as an indicator for all the tests carried out is founded on the provisions of ASTM Classification of silica refractory [146], which classified silica refractory based on minimum MOR of 3.45MPa and specified that the purity of the silica raw material used should be determined by XRF.

Table 3.4: Composition of seven 15g refractory powder mix samples fired at 1350°C

Sample Label	Proportion of mineralizer (wt.%)
A	0
B	0.6
C	1.0
D	1.4
E	1.8
F	2.6
G	3.4

3.4.2.2 Optimal Compaction Pressure Determination

The optimum ratio of the mineralizer to the RHS in a batch as determined from the procedure described under section 3.4.2.1 was used to mix powders in this step. The mixed powders were compacted with pressures ranging from 30 to 150 MPa inclusive to form the refractory test bars of dimensions of 35 x 9 x 6 mm^3. The green compacted bars were fired at 1350°C and tested for modulus of rupture.

3.4.2.3 Determination of Optimal Firing Temperature

Silica refractory is quite fragile and delicate to handle. For easy handling of the refractory, it is first pre-fired for it to gain strength. This strength comes as a result of the phases that are formed within the refractory. From the literature review, it was established that phase transformation becomes pronounced in the RHS at from 900 °C. Since a dopant is used, it was necessary to lower the investigation temperature to below 900°C. This is the reason why 850°C was selected as the starting firing temperature. Literature has also shown that at temperature of 1470°C, tridymite completely transforms to cristobalite. Like is known in the refractory industry, it is the presence of tridymite that reinforces the refractory and so, it was wise to fix the upper temperature limit of investigation at 1450°C. For uniformity, interval of 100°C was chosen.

Table 3.5: Firing regime used to determine the optimum firing temperature required to produce silica refractory samples from RH doped with 1.4 wt.% $Ca(OH)_2$, soaked for 6 h.

Sample Label	Firing Temperature (^{0}C)
A	850
B	950
C	1050
D	1150
E	1250
F	1350
G	1450

3.4.2.4 Refractory Characterization

The MOR tests were performed in line with the prescription of ASTM 133 [156], using a 5kN universal testing machine (Lloyd Instruments, model LR-5K). The cross head speed was set to 0.5 mm/min. The boiling water method described in ASTM C20 [143] was used to perform apparent porosity (AP) and bulk density (BD) tests. For the thermal expansion studies, a Shinku-Riko LIX laser interferometric dilatometer was used and it gave plots of the thermal expansion and coefficients of thermal expansion of the samples at different temperatures, ranging from 25 to 1500 °C. X-ray diffractometer (XRD) (Bruker D8 Advance, Germany) was used to determine the mineralogical composition and phase transitions in the fired refractory. Each specimen was scanned in a range of $2° \leq 2\theta \leq 80°$ at a scanning speed of 4°/min. Morphology was imaged with Zeiss Supra 55VP Variable Pressure Field Emission Scanning Electron Microscope (VP- FESEM), which also revealed the particle sizes of the samples.

3.5 Chapter Summary

The various methods to accomplish the planned experiments which are targeted at achieving the objectives of this research as laid out in section 1.4 have been discussed in this chapter. Chapter 4 presents the experimental results and their discussions.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Chapter Overview

This chapter presents and discusses the results obtained from the various tests undertaken in this research. It is structured in line with the objectives of this research, which are as laid out in section 1.4. Thus, three sections are presented and discussed. The first part, Section 4.2 presents findings and discussion on the production, characterization and optimization of the production and effects of HTB process parameters of RHS. The second part, Section 4.3 reports and discusses results on the production process parameters optimization of RHS refractory while the last part, section 4.4 of the work is dedicated to property evolution in the RHS refractory produced in this research.

4.2 Production of Silica from Rice Husk: Process Development and Product Characteristics

This section discusses findings arising from the design of HTB process reactor, application of same in the purification treatment process of rice husk and finally, the characterization of the obtained silica from the process, in order to optimize the production process.

4.2.1 Reactor Calculated Dimensions

Evaluating equation 3.1 given the conditions and material properties specified in section 3.2.1, a cylinder wall thickness of $t = r_1 - r_2 = 4.49$ mm was obtained. However, 6mm was used for design convenience. In the same vein, equation 3.2 yielded $t_1 = 6.26$

mm, when a material factor, $k_I= 0.35$ was used. However, in the design, the cover and base thicknesses were taken as 15 mm and 30 mm respectively, due to some other aesthetic considerations. When equation 3.3 was evaluated in combination with equation 3.5 for the bolts, a stress level of 20.78MPa was obtained for M10 bolts and since this stress level is lower than the allowable stress of 43.00MPa in the bolt material under the design conditions, it was deemed safe for use. The quantity of heat needed to heat up the system (reactor and content) from room temperature to 300°C was calculated to be Q=600,495J. This calculation was based on equation 3.6 and the conditions set out in section 3.2.1.4. Using an oven which had power capacity of 2000W, it took approximately 5 minutes for heating up the reactor and its content to 300°C. This is in agreement with the expression given for time to heat up the system, explained in section 3.2.1.4.

It must be stated at this juncture that in the design process, preference was given to small reactor cavity diameter than a big one because large diameters would result in higher stress on cylinder cover and the securing bolts, requiring more material usage. This is what preliminary trials tests of the earlier designed and fabricated versions of the reactor yielded. The picture of the designed reactor is shown in Figure 4.1.

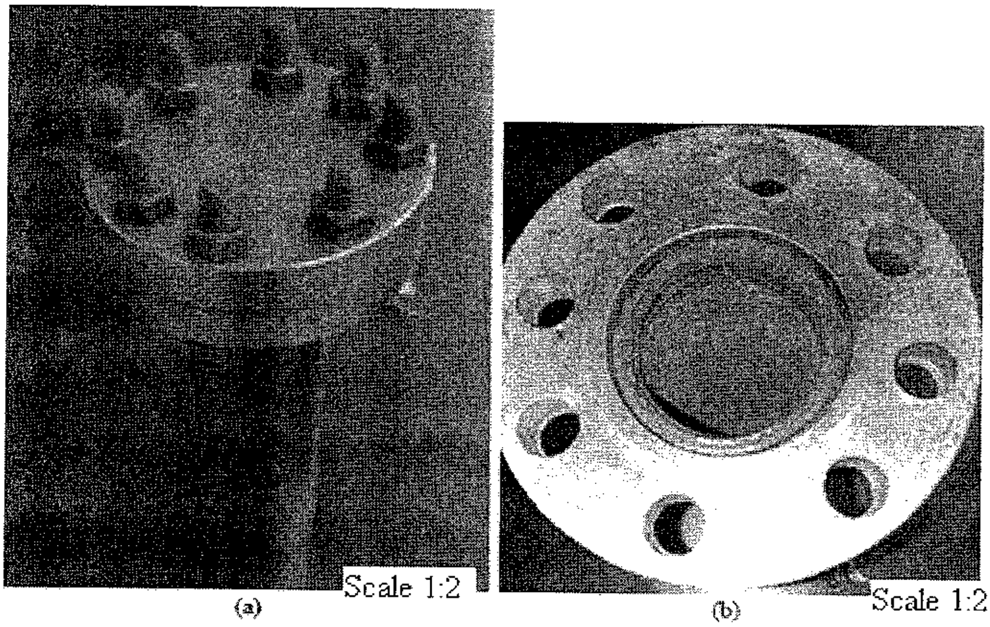
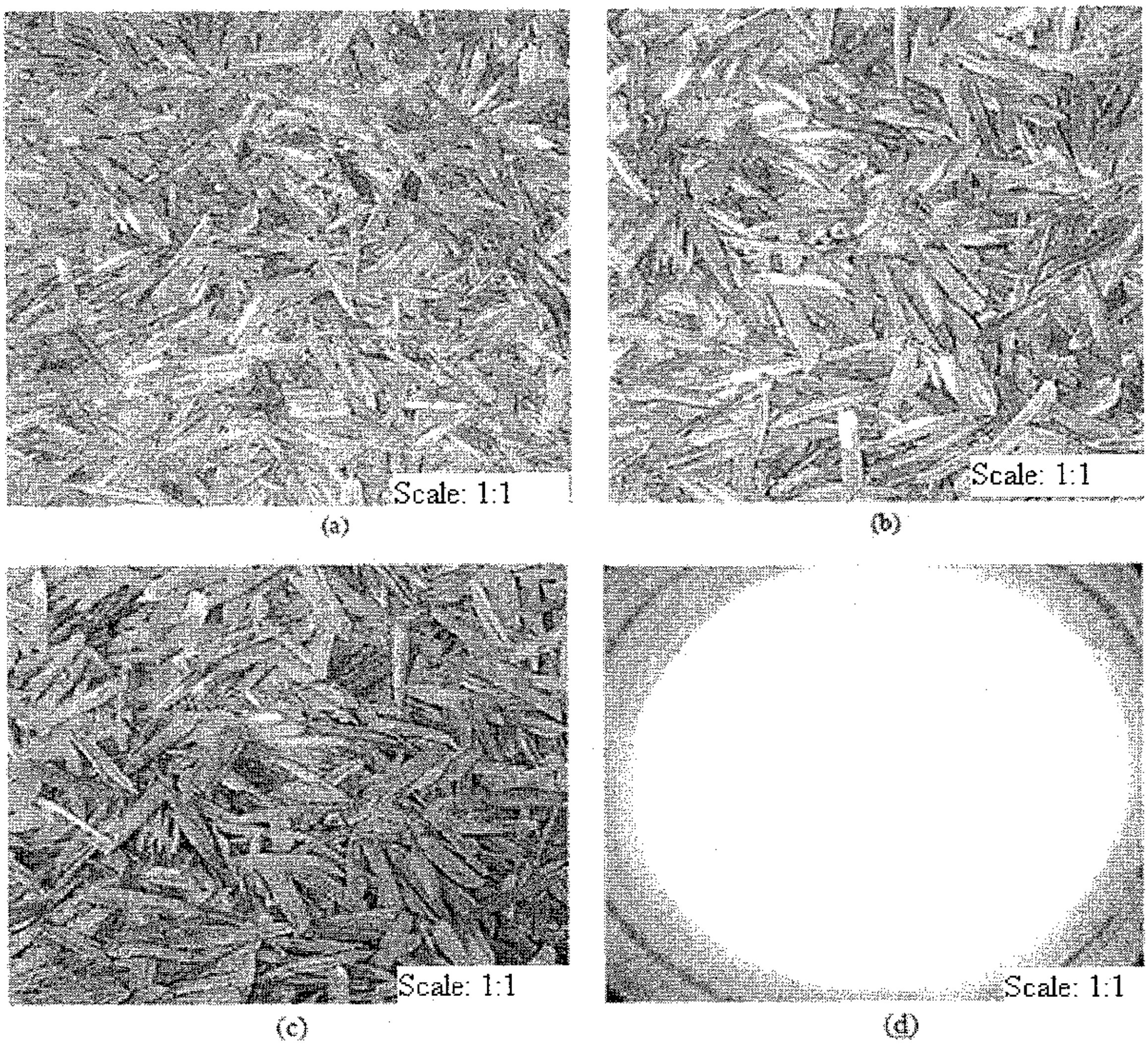


Figure 4.1: Picture showing (a) the designed and assembled reactor (b) the cavity of the reactor

4.2.2 The Transformation of the Raw Rice Husk to the Product (RHS)

The pictures for the rice husk as it transforms from "as received" to the final product (white rice husk silica otherwise known as RHS) are shown in Figure 4.2.



(a) (b) (c) (d)

Figure 4.2: Transformation of rice husk from (a) as received (dirty) sample to (b) washed and wet sample, (c) HTB processed husk awaiting incineration (d) obtained high purity RHS.

The washing step took away the dust and sand particles in the as received samples, while the HTB process leach off the oxide impurities and the lignocellulosic materials in the husk. The HTB process also help to pyrolize the husk, thereby reducing the amount of time needed during the incineration step, which transforms the husk from the the pyrolized state to the white RHS.

4.2.3 The Optimized Process

The process of optimization was divided into two parts: the use of the one-variable-at-a-time (OVAT) method and thereafter the deployment of the factorial method. These two shall be discussed in the sections that follow. The purpose of the OVAT has been explained in section 3.3.2.3.

4.2.3.1 The OVAT Method outcome

The parameters that were investigated were: (i) water to husk ratio (WTHR), (ii) temperature (TEMP) and (iii) soaking time (SOKT). The reasons for choosing these parameters have been explained in section 3.3.2.3. The essence of using the OVAT method was to determine the effect of each variable on the properties of the silica produced, especially the determination of how they affect the purity of the obtained RHS using the HTB process. The second reason as explained in section 3.3.2.3 wass to use it to determine the lower and upper limit of the factors under investigation (WTHR, TEMP and SOKT), which are needed for successful implementation of complete optimization of the HTB process using the factorial method of design of experiments.

The results obtained for the WTHR factor are presented in Figure 4.3. The trend is clear, rising from 1g/ 70 ml to peak at 7g/ 70 ml and decreased thereafter. This result suggests that for best process performance, 1g of rice husk requires 10 ml of water. This is in sharp contrast to the acid leaching process, where a minimum of 500 ml of acid is required to reflux 5g of rice husk, which would still further require treatment with concentrated alkali [157].

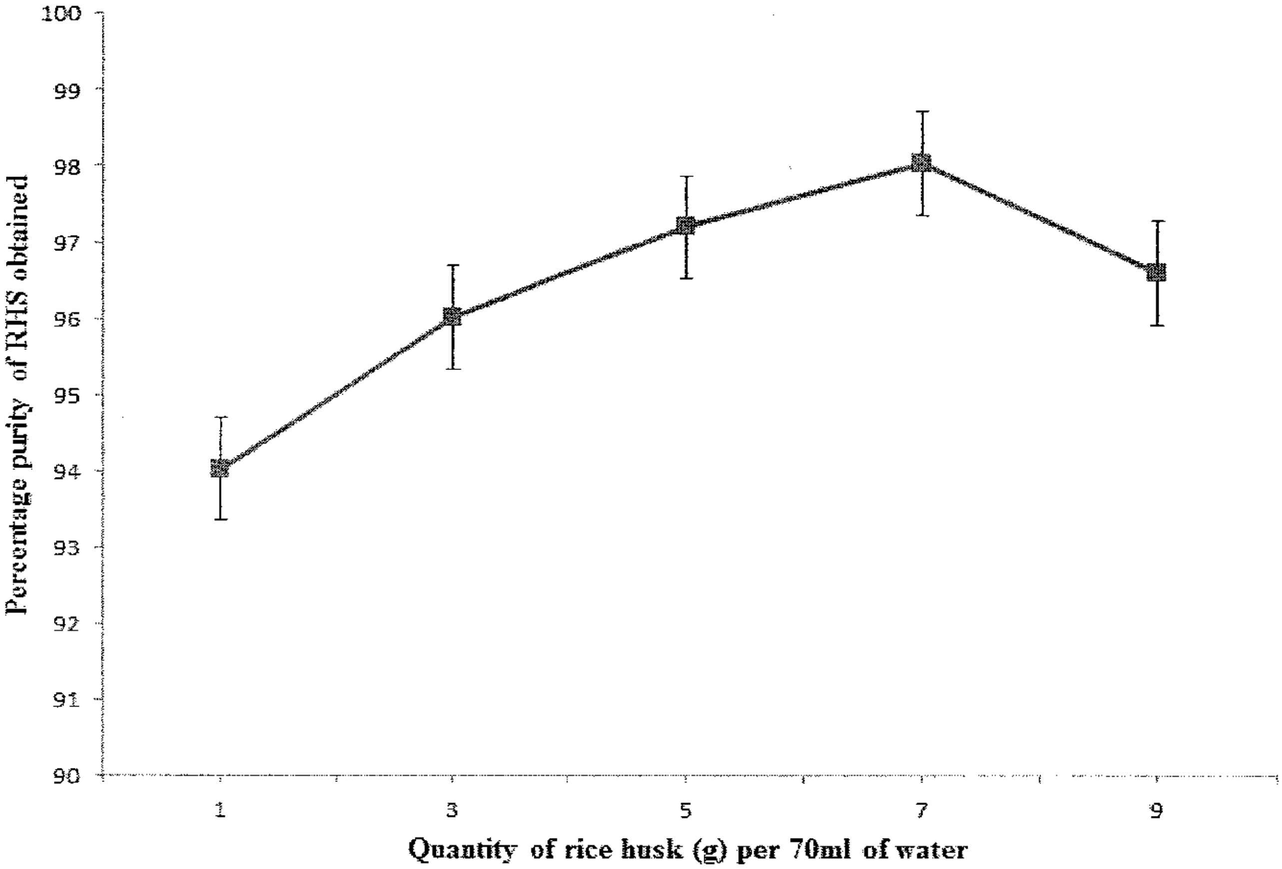


Figure 4.3: Relationship between percentage silica in ash versus weight per volume ratio of rice husk and water.

While the results obtained were clear for the ratio of rice husk quantity to 70ml water (which are graphically presented in Figure 4.3), they were not as straight forward for other factors- temperature and soaking time. The results for effect of temperature and soaking time on the purity of RHS are shown in Figures 4.4 and 4.5 respectively.

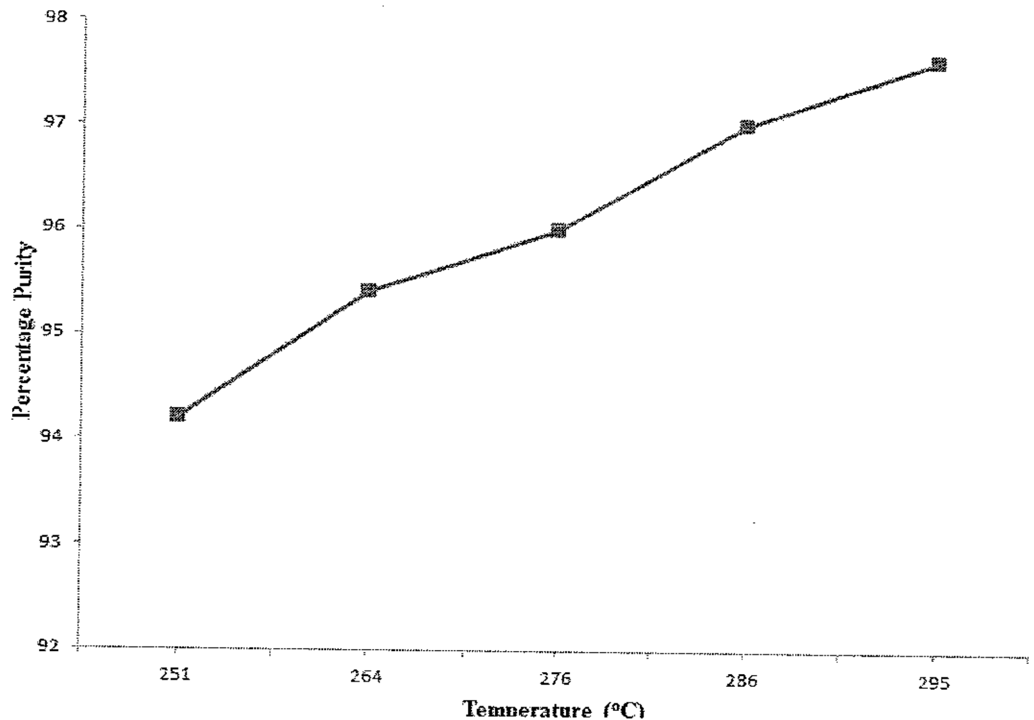


Figure 4.4: Effect of temperature on the purity of RHS

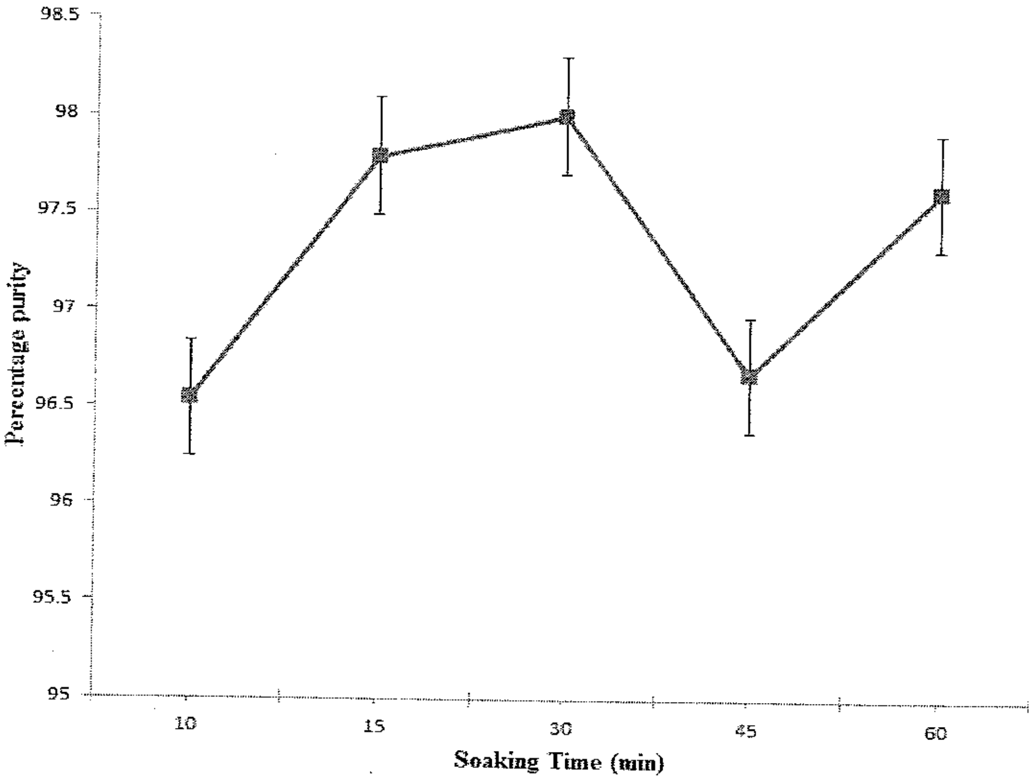


Figure 4.5: Effect of soaking time on the purity of RHS

This sort of situation usually arises when factors that are being investigated share some interactions with one another. In such a case, a change in one of the factors would affect the other. The optimal values for such interacting factors cannot be determined except when factorial or other process optimization technique is employed. In this research, the factorial method was chosen for the optimization process. It was chosen because the factors investigated were three in number and the behavior of these factors was fairly known from the relationships shown in Figures 4.3 through Figure 4.5.

In the use of factorial design of experiment to optimize a production process, after the factors have been identified, the next step is to choose the minimum and maximum levels of each of these factors to be used in the factorial method of experiment design. From Figure 4.3, it was clear that the highest purity obtainable occurred at a ratio of 7g rice husk per 70 ml of water. The target purity level was set not to be less than 97 percent (as required in silica refractory manufacture). From the graph, ratios less than 5g of husk to 70 ml of water yielded purity percentages below the target level of 97 percent. For this reason, the minimum and maximum levels of WTHR were chosen as 5g/ 70ml and 7g/70ml respectively.

As regards the temperature, a continuous rise in percentage purity was witnessed as shown in Figure 4.4. There seemed to be no clear point to determine what values may be optimal for this factor. However, reactor design restricts the maximum operational temperature to 300°C (see section 3.2.1). Therefore, the maximum temperature level is chosen to be 295°C, which is a little less than 300°C. Also, since the RHS purity obtained through the use of 264°C was about 96%, it was set as the minimum threshold temperature. This decision was favoured due to the fact that there may be some interaction between this factor and the soaking time, since the graph of effect of SOKT on purity (Figure 4.5) yields a dome between 15 and 30 minutes of soaking and then a fall. As noticed from Figure 4.5, there is a rise in RHS purity after 45 minutes of soaking. What this suggests is that somewhere between 15 minutes and 45 minutes of soaking, there must be an optimum value of soaking time. Therefore, the minimum and maximum values of soak time chosen for the factorial step were respectively, 15 and 45 minutes.

These chosen minimum and maximum levels of the factors- WTHR, TEMP and SOKT- were used to construct the factorial matrix shown in Table 3.2, which has been used to perform the 2-level factorial design of experiments shown in Table 4.1.

4.2.3.2 The Factorial Method outcome

Using the 2-level matrix presented in Table 3.2 and knowing that three factors are being evaluated, Table 4.1 was constructed, having eight runs. As explained in section 3.3.2.3, the response chosen is the percentage purity of the RHS, determined by XRF. The average of the three replications obtained for the responses of each run is shown in Table 4.1.

Table 4.1: Average response of each experimental run

Variable			Response
TEMP (^{0}C)	WTHR (g/70mL)	SOKT(min)	Silica purity (%)
295.00	5.00	15.00	95.7
264.00	7.00	15.00	95.3
264.00	5.00	15.00	94.5
264.00	5.00	45.00	95
295.00	7.00	15.00	98
264.00	7.00	45.00	96
295.00	7.00	45.00	98.9
295.00	5.00	45.00	97

This combination of levels of the process factors with the matching responses were fed into the design of experiment software- Design Expert ® Software, version 6.0 and analyzed. The statistics shown in Table 4.2 were obtained on performing analysis of variance on the data shown in Table 4.1.

Table 4.2: Analysis of variance for the model

Parameter	F-value	Probability > F	Remark
Model	15.34	0.0245	Significant
A	37.71	0.0087	Significant
B	17.53	0.0248	Significant
C	5.63	0.0983	Insignificant
AC	0.49	0.5355	Insignificant

The analysis yielded a "Pred R-Squared" of 0.6685, which is not as close to the "Adj R-Squared" of 0.8912 as one might normally expect. This may indicate an assignable problem with the response data obtained, as the washing step in the process of experimentation was not initially considered as very important, but has turned out to be so. A longer washing period of say, about 5 minutes, leads to the dissolution in water of P_2O_5 reamining in the pyrolised husk. This drastically improved the the purity, and as could be observed, the purity reported (Table 3.3) for the RHS used in the production of the refractory samples was 99.04 percent, higher than the one obtained in any of the runs' results reported in Table 4.1, due to this reason.

As shown in Table 4.2, the Model F-value of 15.34 implies the model is significant and that there is only a 2.45% chance that a "Model F-Value" this large could occur due to noise.

When the system was optimized using the software quoted above, it yielded most desirable optimal values for the process variables as follows: TEMP = 286.13; WTHR= 6.98 and SOKT= 15.68, indicating that unduly high soaking time is counter-productive. Such negative effects were noticed in the colour and value of the residual carbon in the obtained rice husk silica, as discussed in section 4.2.5.

4.2.4 Analysis of the Effectiveness of the HTB Process in Purifying RHS

Metallic impurities have adverse effects on the various applications into which rice husk silica might be put. One of the reasons why it is difficult to obtain silica with purity in excess of 97% from rice husk by the direct incineration process is a consequence of the effects of the metallic impurities the husks contain. For instance, it has been reported by Chandrasekhar *et al.* [105] that alkali oxides, especially K_2O impart black colour on the particles. Some explanations to support this phenomenon is that there exists a strong interaction between alkali oxides, especially oxides of potassium and sodium, contained in rice husk and the silica therein, such that they can result in the surface melting of SiO_2 particles and accelerate the early crystallization of amorphous SiO_2 into cristobalite, as implied by research results [23, 106]. This was one of the reasons why Kalapathy *et al.* [108], could not achieve purity of up to 98% even after 14 hours of their sol-gel treatment of rice husk ash, with bases and acids. This surface melting of these oxides on the silica grossly reduces the surface area, thereby reducing the reactivity of the particles. For this purpose, it is often necessary to use some pre-treatment methods (which can either be done through acidic or basic medium), to reduce or remove metallic impurities, in order to increase the chances of obtaining silica of higher purity and surface area than is achievable in the direct incineration method. This is why the hydro thermo-baric process was introduced. Table 4.3 shows the chemical composition (analysed by x-ray fluorescence, XRF) of the untreated rice husk (UTD00), the treated rice husk processed at the optimal values of the process factors- TEMP= 287°C; WTHR= 7g/ 70ml and SOKT= 16 minutes. Note: Table 3.3 was extracted from the data in this Table.

Table 4.3 has evidently demonstrated that the hydro thermo-baric process is effective in purifying silica obtained from rice husk. It was found that most of the impurities existing in the rice husk were removed after about 16 minutes of hydro thermo-baric treatment and that only the oxide of phosphorous tended to remain in the solid phase in large quantities. However, when the treated rice husk was sufficiently washed with water after the HTB treatment process before incineration, most of the phosphorus oxide was washed off.

Table 4.3: Chemical composition of the untreated and treated rice husk silica

Item	Untreated	Treated
	UTD00	HTB (Optimum)
SiO_2	91.25	99.04
K_2O	3.829	0.111
P_2O_5	2.45	0.376
CaO	0.875	0.180
SO_3	0.661	0
MgO	0.573	0
Al_2O_3	0.18	0.210
Fe_2O_3	0.0866	0.0829
MnO	0.0726	0
Rb_2O	0.0143	0
ZnO	0.0111	0

As noted by earlier researchers [158], it is suspected that some reactions, such as recrystallization, may have occurred in the process and fixed this oxide (P_2O_5) impurity, but a more detailed investigation which is outside the scope of this research (see section 1.5) is needed to clarify the dissolution mechanisms of this species. Generally speaking, the hydro thermo-baric process has greater promise than any of the methods that previous studies on the removal of impurities with hydrochloric acid at its boiling point have reported, especially those reported by Real *et al.* [159]. This prospect is so because the hydro thermo-baric process results in the reduction in number of steps and unit operations involved in the chemical processes literature has hitherto reported. As noted by Yalcin and Sevinc [24], using water to purify the rice husk silica remains the cheapest. It is noteworthy that the results of these cited previous works also reported difficulties in eliminating some impurities, especially the oxide of aluminium.

4.2.5 Effects of the HTB Process Factors on the Product (RHS)

Having obtained the optimum values of the factors that affect the HTB process (WTHR, TEMP and SOKT), it was necessary to review the effects these factors had on the product (RHS) obtained. Recall that it was clearly demonstrated in Figure 4.3 that the purity of RHS is strongly dependent on the ratio between rice husk quantity (in gram) and water quantity (in milliliter). This dependence gave a clear peak of purity at a ratio of 1g of rice husk to 10ml of water. Beyond this measure, purity decreased. From the optimization values discussed in section 4.2.3, the software yielded 6.98g/ 10 ml as the optimum ratio. This is so close to the value obtained from the OVAT method. Therefore, for convenience, the approximated value of 1g/ 10ml obtained from the OVAT method was used to benchmark the determination of the effects of other factors on the purity of the process.

In the same vein, the factorial process optimization yielded 286.13°C as the optimal value for the temperature. This is approximated to 287°C, since it was not a sound decision to go below the 286.13°C mark. So, what was inportant to investigate was the effect that soaking time had on the quality of the RHS obtained from the HTB process. This is discussed next.

4.2.5.1 The Effects of Soaking Time on Morphology of the RHS

The Field Emission Scanning Electron Microscopy (FESEM) images of the untreated and treated rice husk silica are shown in Figures 4.6 to 4.8. The FESEM images of all the samples before pulverisation- Figures 4.6 (a), 4.7 (a) and 4.8 (a) show flake-like, very disordered structures of a few microns in size. Somehow, these structures are retained in the silica even at the sub-micron level. The pulverised samples depicted by Figures 4.6 (b), 4.7 (b) and 4.8 (b) show very hazy structure of agglomerated submicron-sized particles, with very high porosity as evident in the images. Each micrograph of the after pulverisation samples indicated a composition of particles that is somewhat spherical platelets of sizes in the submicron range. However, HTB-30 sample showed a more agglomerated particle packing and with sizes ranging between 30 and 250nm. Yet even in such agglomerated state, voids could still be observed suggesting that the surfaces of the particles are loosely bound, a condition that indicates it could be highly reactive [16].

The EDX results are shown for samples UTD00, HTB10, HTB15 and HTB30 in Table 4.4.

Table 4.4: EDX analysis of the silica samples

	UTDOO	HTB10	HTB15	HTB30	HTB45	HTB60
Element	Weight%	Weight%	Weight%	Weight%	Weight%	Weight%
C K	25.55	12.02	18.45	31.93	23.97	26.51
O K	30.40	56.63	55.19	52.05	49.99	49.02
Si K	33.97	31.35	26.36	16.03	26.04	24.48
P K	0.79	-	-	-		-
S K	0.57	-	-	-		-
K K	6.21	-	-	-		-
Ca K	1.26	-	-	-		-
Mn K	1.24	-	-	-		-
Totals	100.00	100.00	100.00	100.00		100.00

From Table 4.4, it is clear that the samples of HTB30 possessed more residual carbon than others. Since no other condition has changed but the soaking time, it was safe to conclude that the increase in residual carbon is due to the prolonged heating that has taken place within the reactor. This prolonged heating caused carbonization of the rice husk and at the operating pressure of over 8MPa, the carbon so produced in the process is thought adsorbed to the surface of the silica in an unconfirmed chemical state. This product may be an excellent starting stock for the production of silicon carbide, either in the whiskers or nano-powder form. Therefore, soaking times longer than 16 minutes is unnecessary in the HTB process as this has adverse effect on the quality of the RHS.

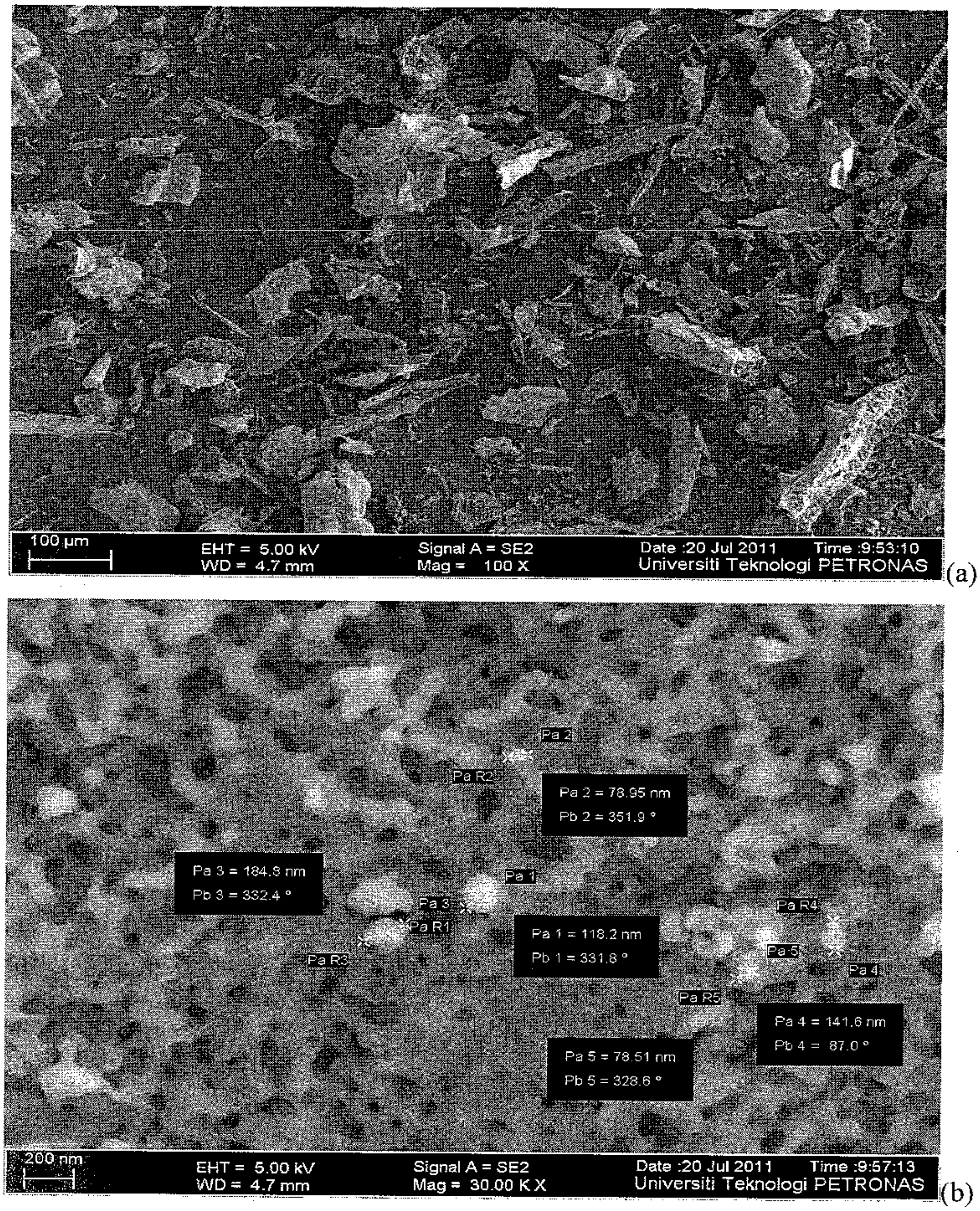


Figure 4.6: FESEM images of silica obtained after incineration (a) untreated sample before pulverisation (b) untreated sample after pulverisation

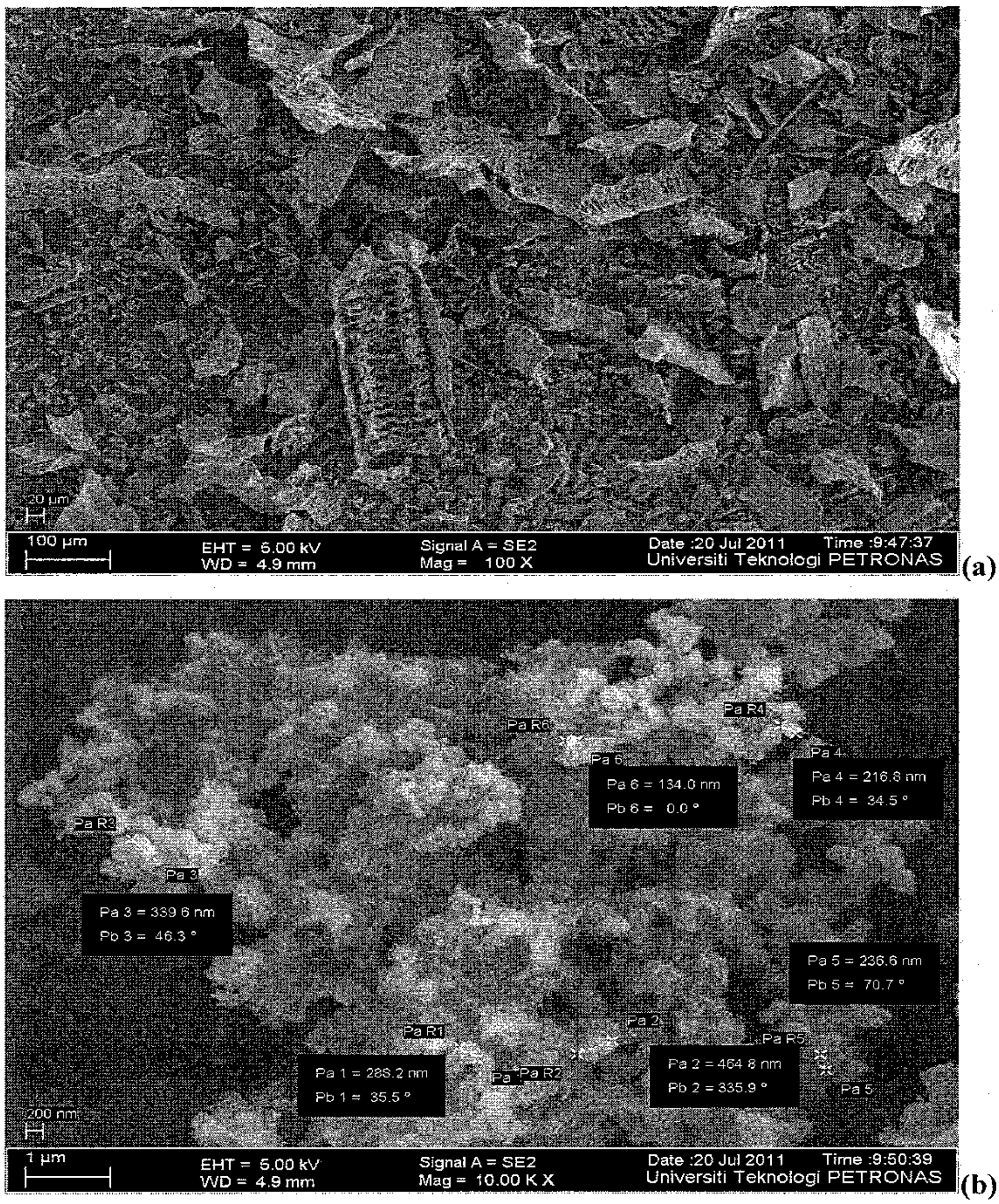


Figure 4.7: FESEM images of silica obtained after incineration (a) HTB-10 before pulverisation (b) HTB-10 after pulverisation

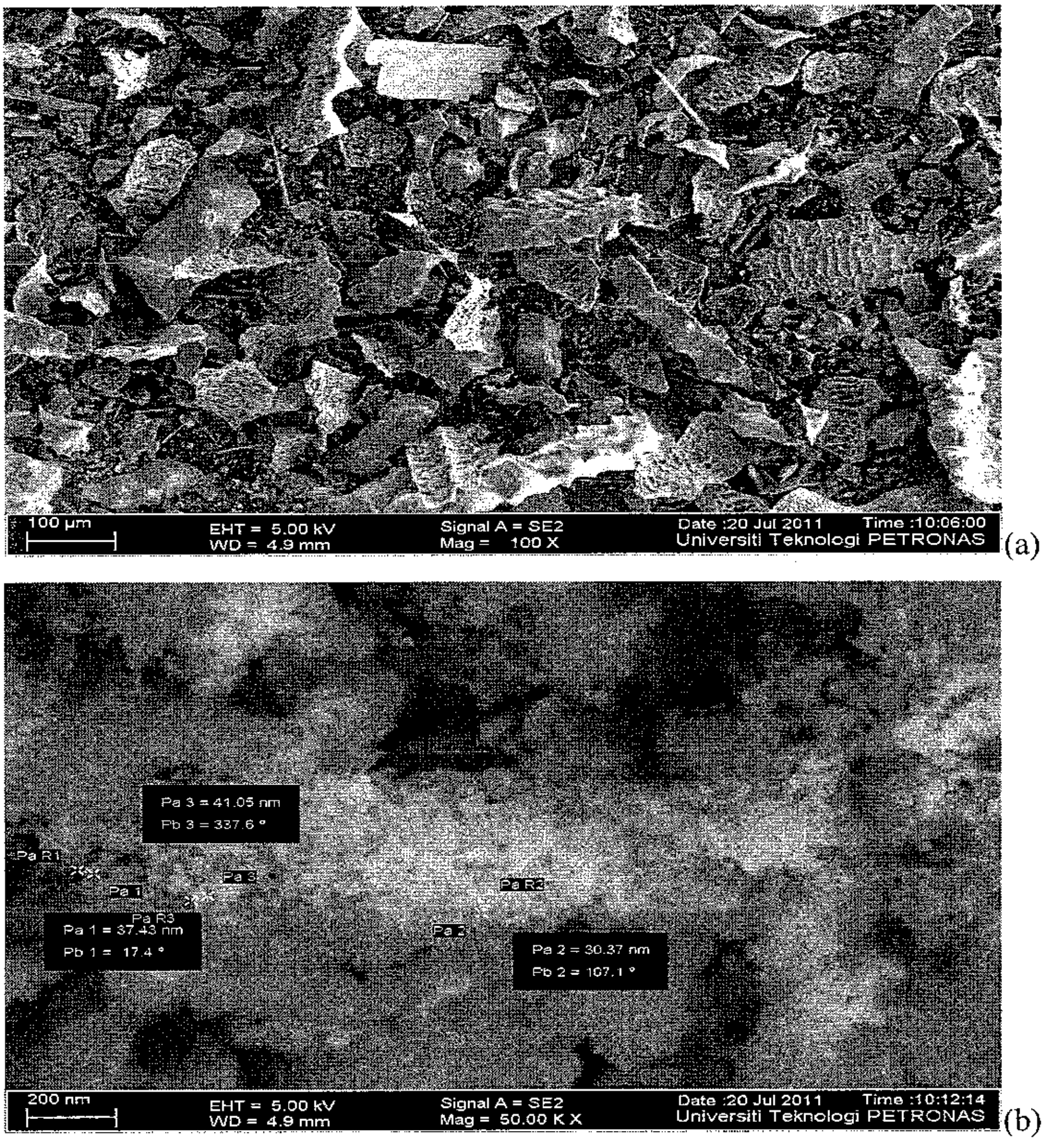


Figure 4.8: FESEM images of silica obtained after incineration (a) HTB-30 before pulverisation (b) HTB-30 after pulverisation.

4.2.5.2 The Effects of Soaking Time on Surface Area and Pore Characteristics

Table 4.5 shows the results for surface area and pore characteristics analysis of the produced rice husk silica. A comparison of the BET result for the three samples indicates a clear increase in the specific surface areas, with the untreated sample having the lowest value of $21.42 m^2/g$, while the HTB30 has a value of $133.94 m^2/g$. It was believed that when the optimized process variables are used, the surface area would greatly increase. What is responsible for this great increase in the specific surface area is that the oxide contaminants in the rice husks are leached away during the hydro thermo-baric process, prior to the breaking up of the organic matter during the thermal decomposition of rice husk, thus leaving a highly porous structure. Also, it is obvious from Table 4.5 that the total pore volume of the untreated sample is 0.0845cm^3/g, much smaller than that of the treated samples, with HTB30 sample having an average value of 0.2813cm^3/g. The average pore diameter (by BET method) of untreated sample is 17.81nm, which is much larger than that of the treated samples, which have an average value of 6.41nm. Thus, it has been demonstrated also that the Hydro thermo-baric process improves the surface area and pore size, hence the reactivity of the produced rice husk silica. Even though literature [22] has reported RHS surface area as high as 235m^2/g, it is highly contestable. No author following the same procedure reported in [22] has got such high results. In fact, Ezzat and Co-workers [157] have repeated same procedures as reported by Liou [22], yet the maximum surface area they reported was 139.8m^2/g. However, the pore volume they reported was much lower (0.00525cm^3/g) than the one obtained from the HTB process.

Table 4.5: Surface area and pore characteristics of the produced rice husk silica

Sample	BET Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm, $4V/A$)
UTD00	21.42	0.0845	17.81
HTB10	99.81	0.2809	9.08
HTB30	133.94	0.2813	6.41

4.2.6 RHS Particle Size Analysis

Fig. 4.9 shows a narrow and unimodal particle size distribution pattern for the tested hydro thermo-baric process purified RHS. It is a representative presentation of the 50 replica tests carried out. From the results, the average particle size of the RHS was determined to be 117 nm. This is the assumed particles size of the RHS used in all other experiments reported in this thesis.

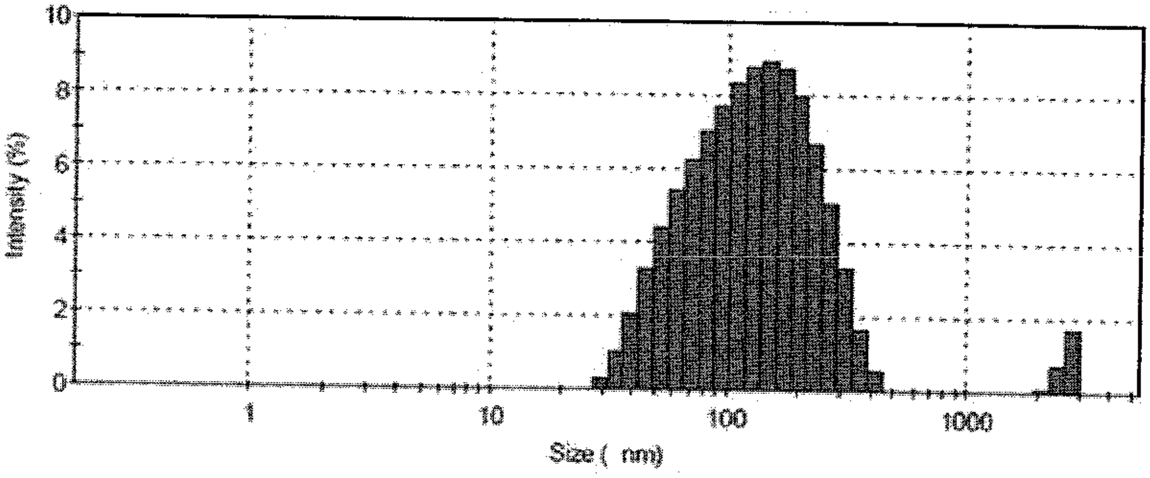


Figure 4.9: Particle size distribution for rice husk silica obtained from the hydro thermo-baric process

4.2.7 Structure of the Silica

The XRD patterns of the RHS are shown in Figures 4.10 (a) UTD00, HTB10 and HTB30 and (b) HTB15, HTB45 and HTB60 samples. The appearance of the diffractograms show diffuse maxima at $2\theta = 23^0$, typical for amorphous silica. This is in agreement with other works [158, 160]. Therefore, it was concluded that the original amorphous structure of the silica obtained from the untreated rice husk (UTD00) is maintained through the structures of the silica obtained from the 10 to 60 minutes hydro thermo-baric treated rice husk (HTB10 to HTB60). Thus, inference drawn from the diffractograms was that within the limits of temperature within which the process is operated, it has no effect on the structure (non-crystalline) of the silica so obtained.

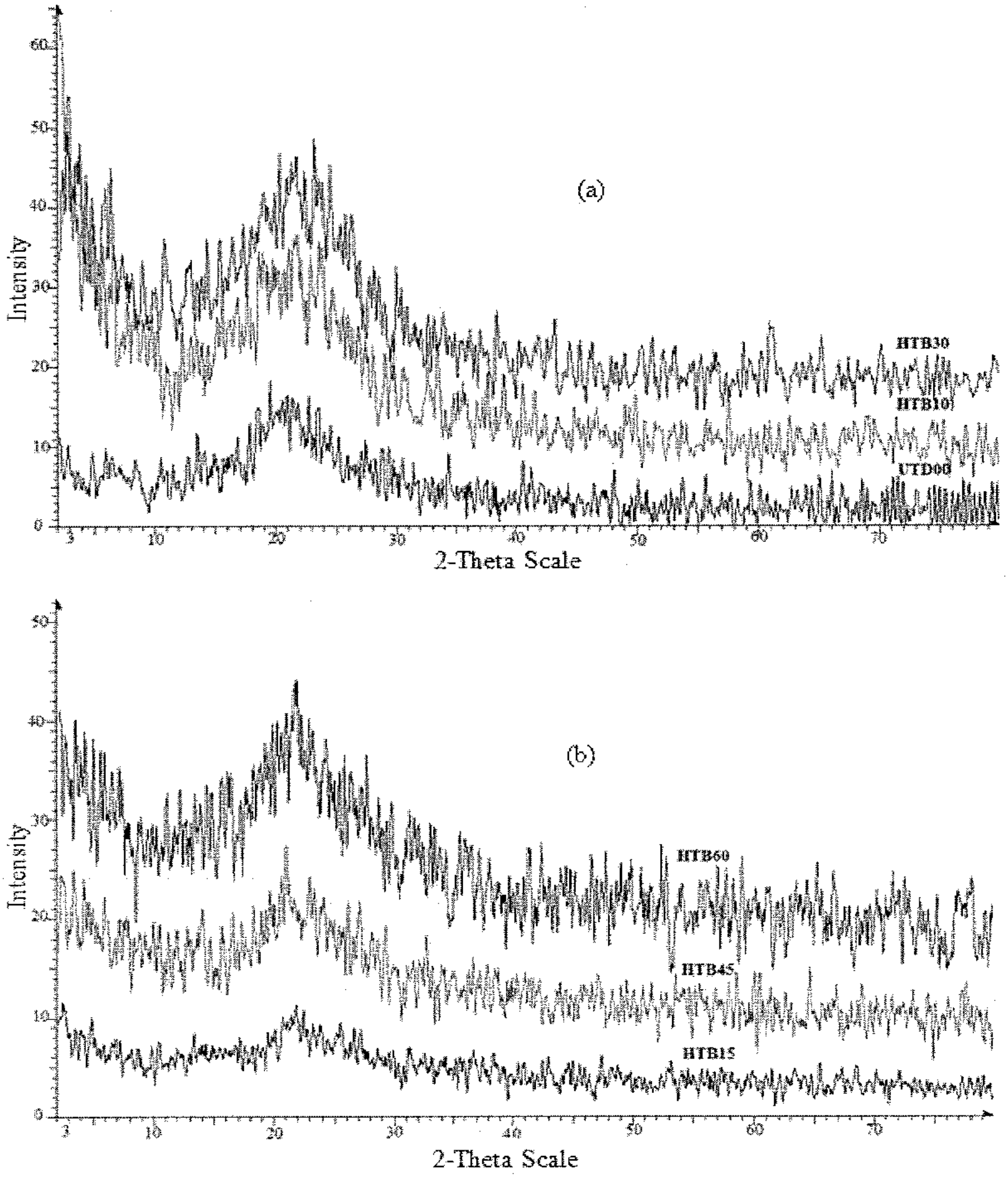


Figure 4.10: X-ray Diffraction patterns of (a) UTD00, HTB10, HTB30 (b) HTB15, HTB45, HTB60

4.2.8 Yield of the Process

The yield of silica from the process is shown in Table 4.6, which directly compares the product of the treated and untreated samples. From the five batches, the product obtained from the treated samples ranged between 18 and 20% of the original starting stock of 5g, compared to the range of values of between 20 and 21% in the case of the untreated samples. Based on the ratio of the grams of ash obtained from each batch of the treated and untreated samples, it was determined that the process gave an average yield of 92.5% of the ash as purified silica. Kalapathy *et al.* [108] obtained a maximum yield of 91% following treatment of rice husk ash with 1N NaOH, after a route consisting of several unit operations and in a period of not less than 14 hours. In similar work, Nittaya and Apinon [120] got a yield of 90.3%, refluxing rice husk ash with boiling 2.5N NaOH. Again, these researchers reported several other processes, that are more complex and environmentally and personnel unkind, lending credence to the advantages of the process developed here.

Table 4.6: Silica yield of the process- treated versus untreated husk

Batch No.	Ash Yield (g)		Percentage Yield ratio
	Treated	Untreated	(treated upon untreated samples)
1	0.9	1.01	89.109
2	0.95	1	95.000
3	0.925	1.05	88.095
4	1	1.025	97.561
5	0.925	1	92.5

4.2.9 Comparative Analysis of Different RHS Production Processes with the HTB Process

In line with section 3.3.3.6, presented in this section are the results of the comparison of the HTB process with other processes in terms of processing time, product structure, yield of the process and product purity.

4.2.9.1 Comparison of Processing Times

The time taken to remove or reduce the impurities in rice husk in order to obtain high purity RHS was considered for each of the processes under review. As shown in

Table 4.7, the HTB process has the shortest processing time of 30 minutes. It was therefore concluded that the process is fast compared to the rest. Thus, the inclusion of the "fast process" in the objective has been justified.

Table 4.7: A comparison of the processing times of different processes

Parameter	**Author**	**Method**	***Processing time (hours)**			**Total time (hours)**
			Pre-treatment	Post-treatment	Others	
Processing time	Current	Hydro thermo-baric	½			½
	Yalcin and Sevinc [24]	Boiling in 3% v/v HCL	2	-		2
	Umeda and Kondoh [112]	Leaching with citric acid at boiling point	1	-	¼ water rinsing	1¼
	Nittaya and Apinon [120]	Precipitation method by boiling in 5N NaOH for hours	3	-		3
	Kalapathy *et al.* [108]	Precipitation and back-titration using concentrated acids and bases	-	1	20	21

*Times shown are those involved in impurity removal from either the raw rice husk or its ash.

4.2.9.2 Comparison of Product Structure

As expected, all the processes compared gave product (RHS) of amorphous structure (Table 4.8). This is because the processes considered were carried out below 700°C, the threshold temperature for the transformation process of amorphous to crystalline structure. Therefore, as argued in section 3.3.2.5, it was safe and scientifically correct to exclude the investigation of varying temperature on the properties of the produced RHS.

Table 4.8: Comparison of effect of processing method on the product structure

Parameter	**Author**	**Method**	**Result**	**Remark**
Structure (either crystalline or amorphous) measured by XRD	Author	Method	Result	Remark
	Current	XRD	Amorphous	
	Yalcin and Sevinc [24]	XRD	Amorphous	
	Umeda and Kondoh [112]	-	Not done	It was not part of research aim
	Nittaya and Apinon [120]	XRD	Amorphous	
	Kalapathy *et al.* [108]	XRD	Amorphous	

4.2.9.3 Comparison of Process Yield

The process yield is an indication of the material wastefulness that results from the use of a given process in purifying rice husk silica. In a nutshell, it is a measure of the process efficiency, when considered in combination with the processing time. The yield of silica from the process is shown in Table 4.9, which directly compares the product of the treated and untreated samples. The average of the yield for the five batches was 92.5% for the treated sample. As is evident from Table 4.9, the yield from the hydro thermo-baric method surpasses several from other processing methods.

Table 4.9: Comparison of process yields

Parameter	**Author**	**Result**
Process yield	Current	92.5
	Yalcin and Sevinc [24]	-
	Umeda and Kondoh [112]	94.6
	Nittaya and Apinon [120]	90.3
	Kalapathy *et al.* [108]	91

4.2.9.4 Comparison of Product Purity

As shown in Table 4.10, the purity of RHS obtained from the HTB process is at par with the ones reported in the cited literature under comparison. The purity is above 99%, which is more than the acceptable limit of 97 or greater percentage purity required for super duty silica refractory manufacture. Though some reported values in literature ([24], [112]) may be higher that the purity of the HTB product, the lesser processing time required still gave comparative advantage to the HTB process.

Table 4.10: Percentage pure silica in the obtained product

Parameter	**Author**	**Method**	**Result (% silica in ash)**
Purity (That is % silica in the product)	Current	XRF	99.04
	Yalcin and Sevinc [24]	Weight loss on volatilization	99.66
	Umeda and Kondoh [112]	XRF	99.77
	Nittaya and Apinon [120]	XRF	98.14
	Kalapathy *et al.* [108]	ICP	93

4.3 RHS Refractory Production and Parameters Optimization

As discussed in section 2.6, refractory characterization is divided into characteristic data properties, design related properties and performance/service related properties. The characterization undertaken in this research relates to the characteristic data properties, which help in the design and manufacture of refractories. Two major indices (MOR and BD) were chosen for the determination of the optimal values of the process parameters under investigation. The decision to choose these two indices stems from the classification method used in the code ASTM C416 [146], which expressly classified silica refractories based on their tested MOR. MOR is affected by BD, which in turn is affected by AP. Depending on temperature, initial firing of refractory often results in liquid phase sintering, which influences porosity. These factors are discussed together in the sections that follow.

4.3.1 Compaction Pressure Effects

Figure 4.11 shows the effects of compaction pressure on the physical properties of the fired RHS refractory. Specifically, its effect on bulk density (BD) is of interest, due to the roles of BD in refractory performance. Therefore, the bulk density of the sintered refractory was extracted and treated in isolation as shown in Figure 4.12. The Figure 4.12 shows a somewhat hyperbolic-quadratic relationship between BD and compaction pressure. As the compaction pressure rose, so did the BD until a certain critical compaction pressure range (between 90 and 110 MPa), where the rise in the value of BD shows a gradual dome, marking a transition between rapid and marginal increase in value.

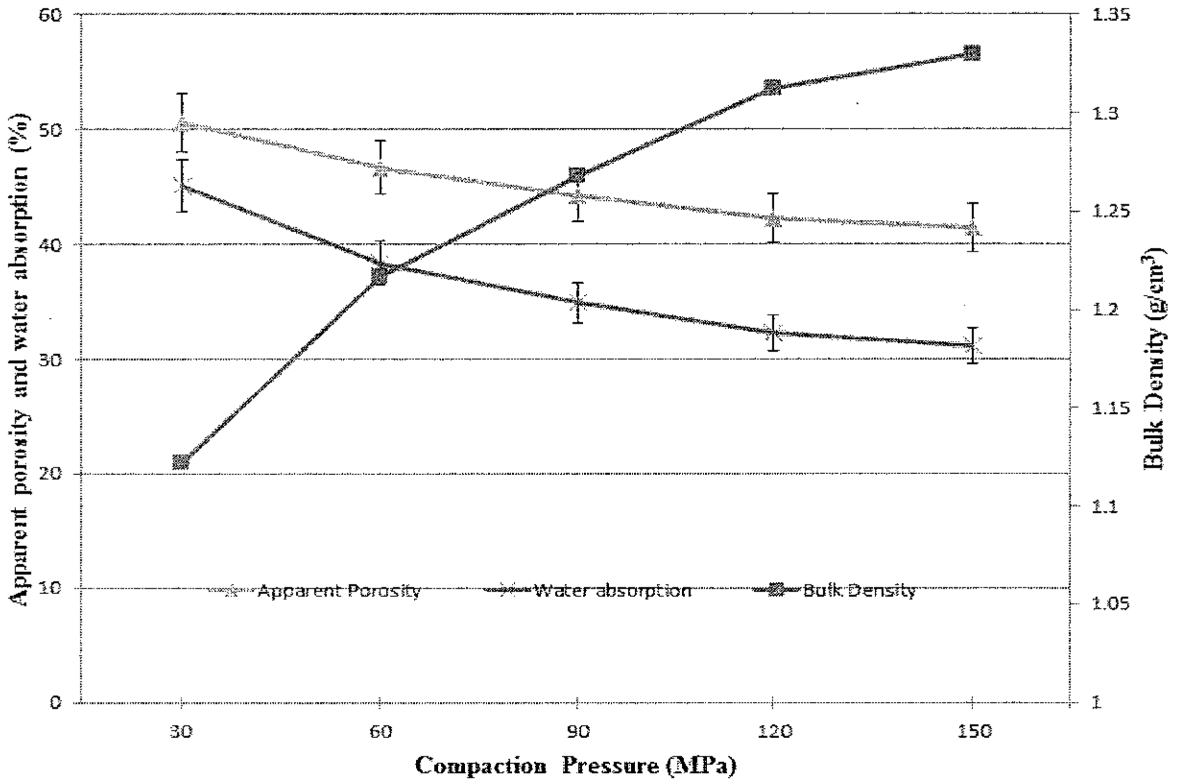


Figure 4.11: Effect of compaction pressure on Apparent porosity, water absortion and bulk density of fired RHS refractory.

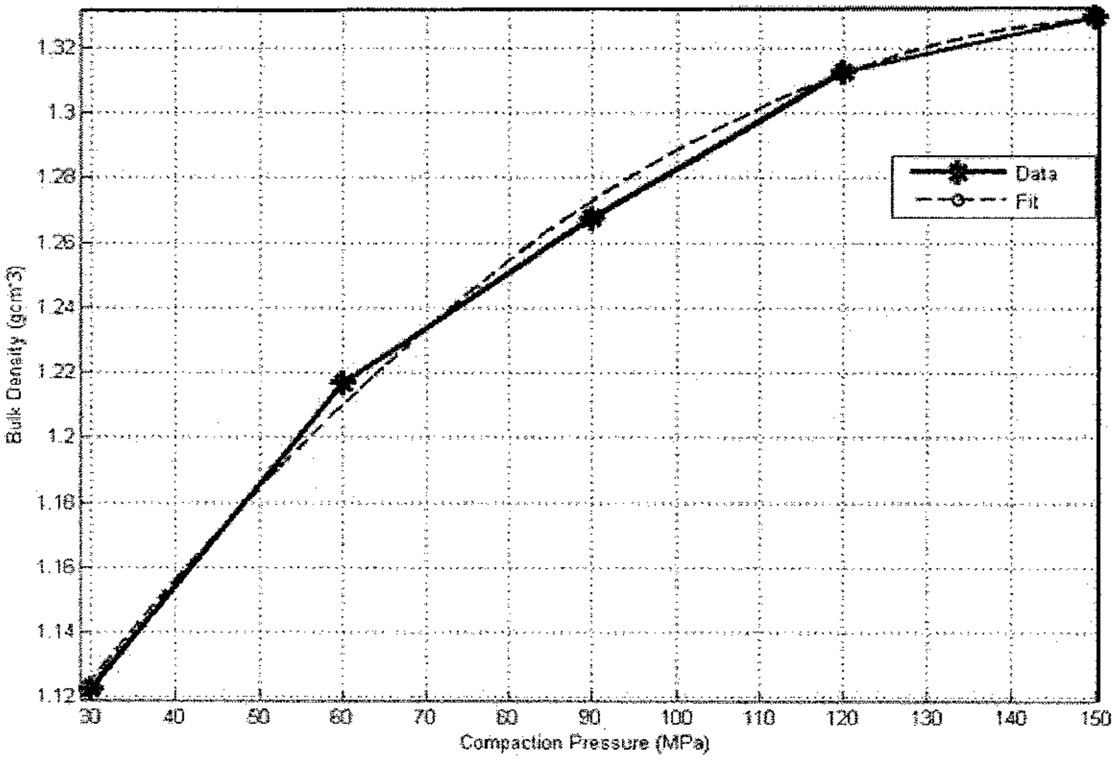


Figure 4.12: Bulk density-Compaction pressure relationship after firing

This realtionship shown in Figure 4.12 was optimised using regression analysis techniques in MATLAB and the following prediction equation for bulk density-compaction pressure relationship was obtained.

$$BD = ax^2 + bx + c \tag{4.1}$$

In equation (4.1), BD=bulk density (gcm^{-3}); x is compaction pressure in MPa and a, b and c are coefficients, having the values: $a = -1.267e^{-005}$; $b = 0.003982$; $c = 1.017$. The goodness of fit for this prediction equation yielded R-square value of 0.9973 and RMSE value of 0.006135. With such a close to unity R-square and very small RMSE, it is certain that equation (4.1) would give a close to true value for BD.

Incidentally, the MOR of the fired refractory increased and peaked in the range of compaction pressure, 90-120 MPa and thereafter, attenuated as shown in Figure 4.13.

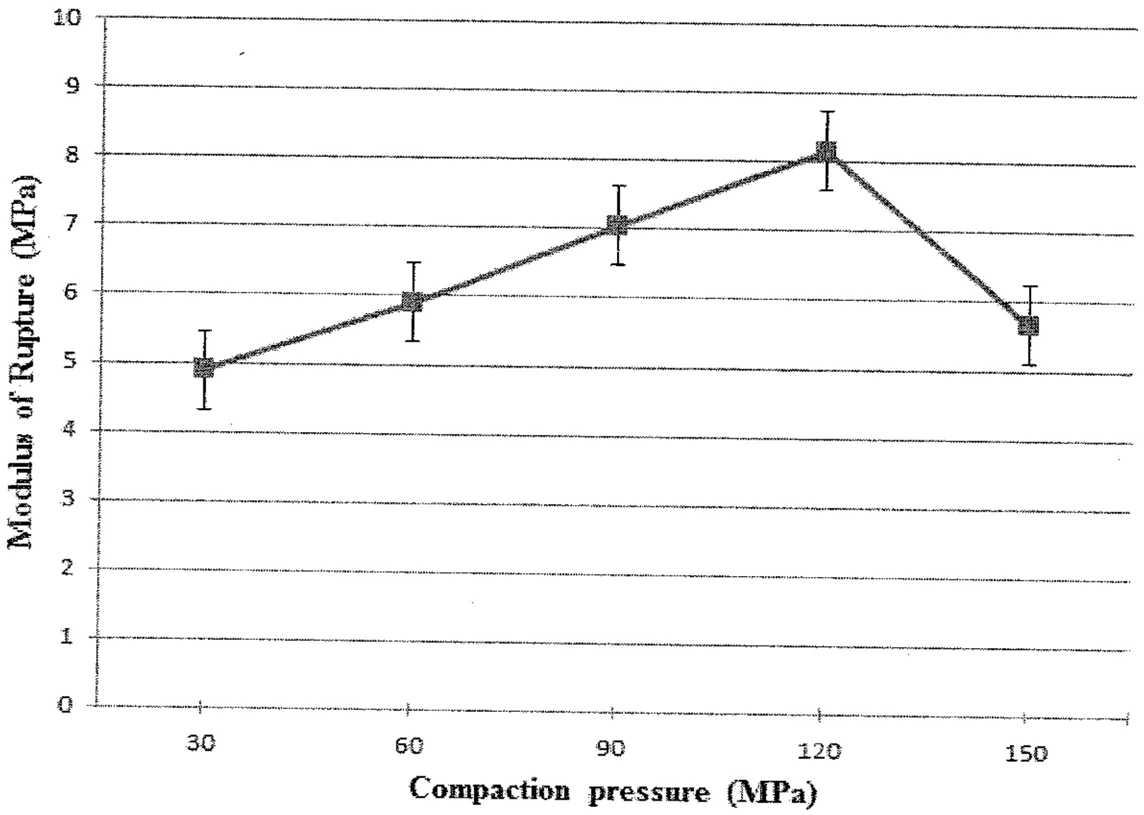


Figure 4.13: Effect of compaction pressure on MOR of sintered refractory

This attenuation in both BD and MOR after the critical pressure range could be explained using Figure 4.14, which shows the ceramic particles covered completely with a PEG layer at the onset of the critical pressure range. As the pressure is increased, the thin film of PEG which originally wraps around the ceramic particles is crushed gradually until the compaction pressure reaches the modulus of elasticity of the PEG. This coincides with critical pressure region. Beyond the critical pressure, this PEG layer is completely crushed and it flows to the exteriors of the green compact bulk, close to the mould-powder boundaries. Thus the boundaries of grain-to-grain are left bare. This has two implications. First, a layering occurs close to and in contact with the mould– powder boundaries. This layer consists of the binder which has flowed out from the depths of the compacted powder and few of the powder particles which are along the boundaries, sheared off from the main compacted body due to high frictional stresses imposed on them by the mould walls (Fig. 4.14 (a)). Secondly, as a result of the flowed out binder, grain-to-grain contact occurs (as depicted in Fig. 4.14 (b)), which in turn causes micro- distortion of crystal layers.

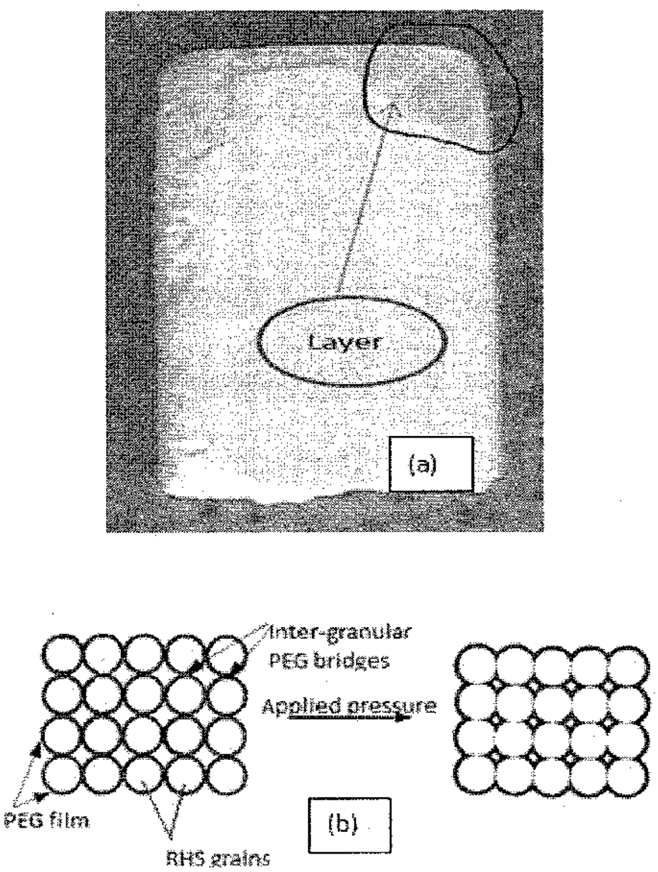


Figure 4.14: Interaction between RHS grains, PEG and compaction pressure

This binder crushing explanation is a function of the hardness, H, of the binder used in the system. Studies have shown [161] that for a polymer (like the PEG binder film), hardness of a layer of polymer could be expressed in terms of the Young modulus of the polymer (E_{pol}) as:

$$H \approx 10\left(E_{pot}\right)^{\frac{3}{4}} \tag{4.2}$$

where H and E_{pol} are expressed in MPa and GPa, and stand respectively for hardness and modulus of elasticity of the polymer.

For the polymer, PEG 8000, E_{pol} has been given as 2.2 GPa [162] and using this value in equation (4.2), yields a crushing pressure of approximately 101.58 MPa. This is the region of the critical pressure that manufacturers could work around for RHS production using PEG 8000 as binder. From the discussion therefore, it is obvious that should another type of binder be used in the system, it would present a different critical compaction pressure range, as the young modulus of one binder differs from another.

The following deductions could be made from the graphs and discussion:

1) The critical pressure for manufacturing RHS refractory falls in the range of 90 to 110 MPa.
2) There is an attenuated character of densification with increasing compaction pressure beyond this critical range that is, there is only a relatively small overall densification effects in the pressure range beyond 100 to 110 MPa;
3) Beyond the critical compaction pressure range, the occurrence of grain-to-grain contact results in saturation of the crystal lattice of the binder with micro-distortions occurring, causing it to flow to the mould-powder boundaries, with an attendant formation of a layer.

Therefore, the optimal compaction pressure for the production of RHS refractory should be chosen from the range 90-110 MPa, should PEG be used as binder.

While the BD and MOR increased with rise in pressure, there is a reverse trend in the associated fired linear shrinkage of the refractories as shown in Figure 4.15. This reduction in percentage linear shrinkage, which is sharp for pressures lower than the critical range, but very gradual or almost constant after the critical pressure range could be explained as an attendant consequence of the decrease in porosity of the refractory body with increase in compaction pressure (Figure 4.15 (b)), which allows for better bonding in the system.

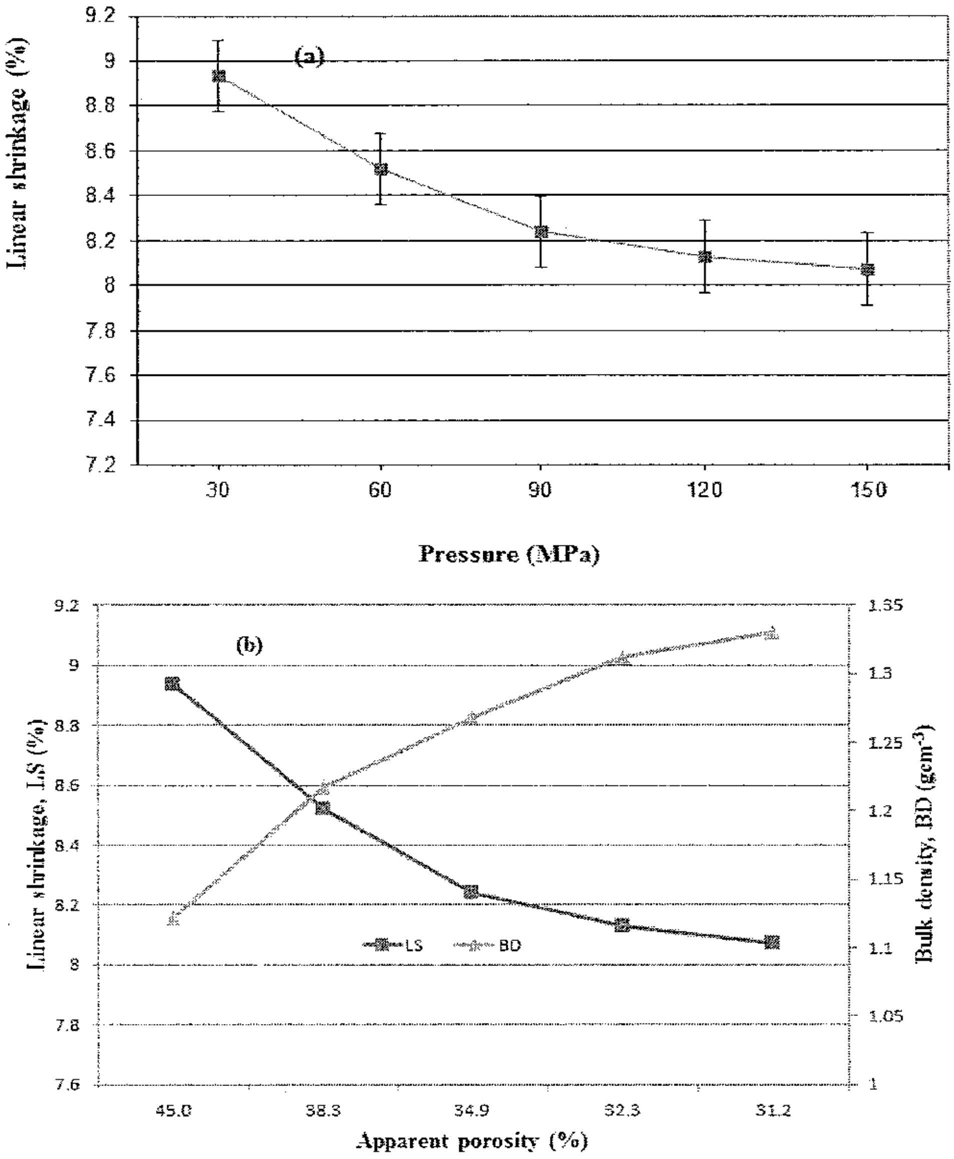


Figure 4.15: Fired linear shrinkage as a function of (a) compaction pressure (b) apparent porosity

The bulk density shares an inverse relationship with apparent porosity as revealed in Figure 4.15 (b), same trend for the modulus of rupture.

4.3.2 Effect of Mineralizer on Physical Properties of RHS Refractory

Figure 4.16 shows the effects of mineralizer on the bulk density and percentage linear shrinkage of RHS refractory. The linear shrinkage is noticed to decrease drastically with increase in the mineralizer concentration until a critical value of 1.4 wt. % of the mineralizer. Beyond this point, there seems to be marginal effects noticeable on both the percentage linear shrinkage and bulk density.

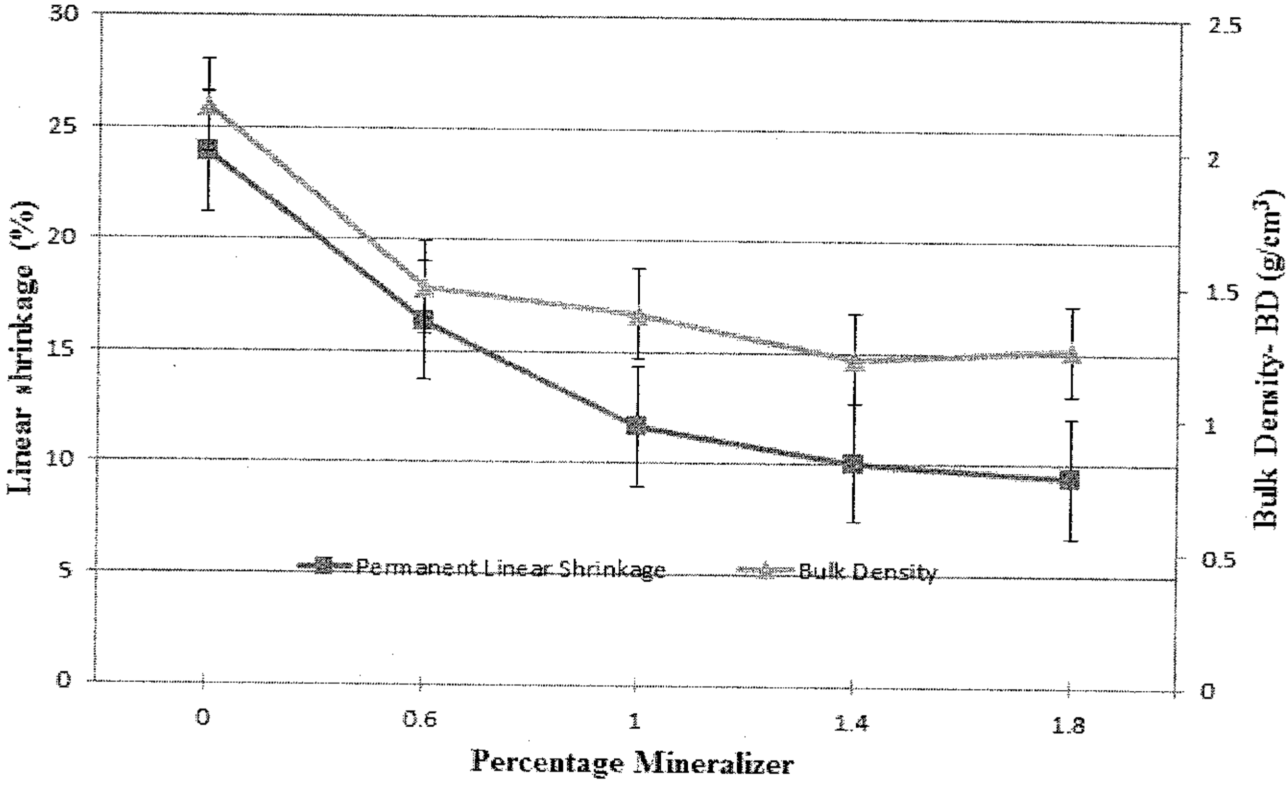


Figure 4.16: Effects of mineralizer on bulk density and linear shrinkage

The cause of this observed trend can be explained through monitoring of the phases formed in the refractory. Recall that the RHS refractory being discussed were fired at 1350°C. At this temperature, several phases had been formed, depending on the quantity of $Ca(OH)_2$ with which the RHS was doped. As evident from the micrographs shown in Figure 4.20 (discussed later), liquid phase sintering begins at about 950°C, where anorthite forms and helps seal up much of the void in the refractory body, thus making it a homogeneous whole. It is also thought that there exist a positive contribution of hydraulic cement influence from the synergy existing between P_2O_5 and the dopant, which results in the formation of hydrated calcium silicates [68] phases in the refractory. Beyond 1250°C, wollastonite is formed, which increased in concentration as firing temperature rose. The effects of wollastonite in ceramics manufacture have been established to include stabilization of dimensions of the cermic in which it is present [163]. Thus, it is not surprising that the percentage linear shrinkage became marginal with rise in the concentration of the dopant. However, through some yet unclear mechanisms, at dopant concentration beyond 2.6 %, pseudo-wollastonite is formed. This transition of wollastonite to pseudo-wollastonite may have started much earlier, accompanied by inversions between the silica polymorphs- tridymite, quartz and cristobalite. These transformations affect the mechanical integrity of the refractory, leading to a lower BD and hence, MOR. The effects of such transformations on the thermal shock resistance of the refractory (reported in section 4.4.1) for dopant concentrations of around 1.4 % were observed to be minimal, due to the presence of wollastonite.

4.3.3 Evolution of Properties with Firing Temperature

In the manufacture of shaped refractories, it is necessary to carry out pre-firing in order to enhance easy handling of the refractories without damage to the shapes. The temperature at which these refractory shapes are pre-fired is dependent on the type of refractory and even amongst refractory with same raw material basis, composition would warrant a separate firing regime for them. Silica refractories manufactured from quartzite sources have very low green strength and have to be pre-fired to impart some mechanical properties improvemnet into them. They often undergo complex firing regimes due to the cantakerous phase transformation that occurs in them as a resut of inversions amongst silica polymorphs. It was therefore, necessary to determine the optimal temperature at which the refractories developed from RHS should be fired to improve their handling strength.

As with the effect created by the mineralizer, so was the trend observed for the effects generated by firing temperature on the refractories. As shown in Figure 4.17, the refractories had increased density until the temperature range of 1250 and 1350°C when there was a relatively constant densification effect. It should be mentioned however, that the BD value at 1250°C (1.35 gcm^{-3}) is slightly higher than that observed at 1350°C (1.33 gcm^{-3}). This suggests an increase in volume occurring within the temperature range of 1250 and 1350°C as a result of tridymitization of the refractory body. From 1350°C, a decrease in volume as a result of lattice contraction as tridymite transits to cristobalite was witnessed, so there is a marginal increase in BD (1.36gcm^{-3}). This implies that for production purpose, pre-firing should be done within this temperature range- 1250 to 1350°C.

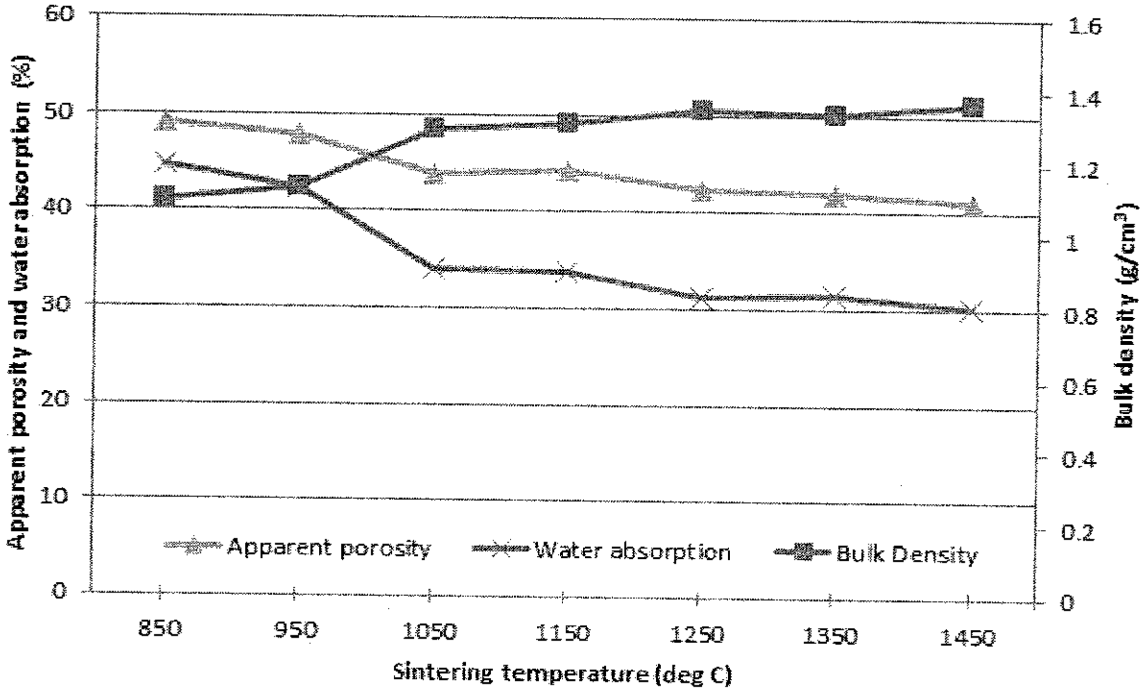


Figure 4.17: Effect of firing temperature on the physical properties of the refractory.

The change in MOR with temperature is shown in Figure 4.18. From the Figure 4.18, it is obvious that MOR of the refractory body shares an inverse relationship with the percentage apparent porosity, with a peak at 1350°C. At 1250°C and beyond, MOR is no longer a function only of the percentage apparent porosity, rather other factors such as the formation of tridymite, visco-elastic effects created as a result of liquid phase sintering and the growth in wollastonite phase. Of these factors, the role played by tridymite is chief and as it transforms into cristobalite after 1350°C, there is a reduction in the MOR.

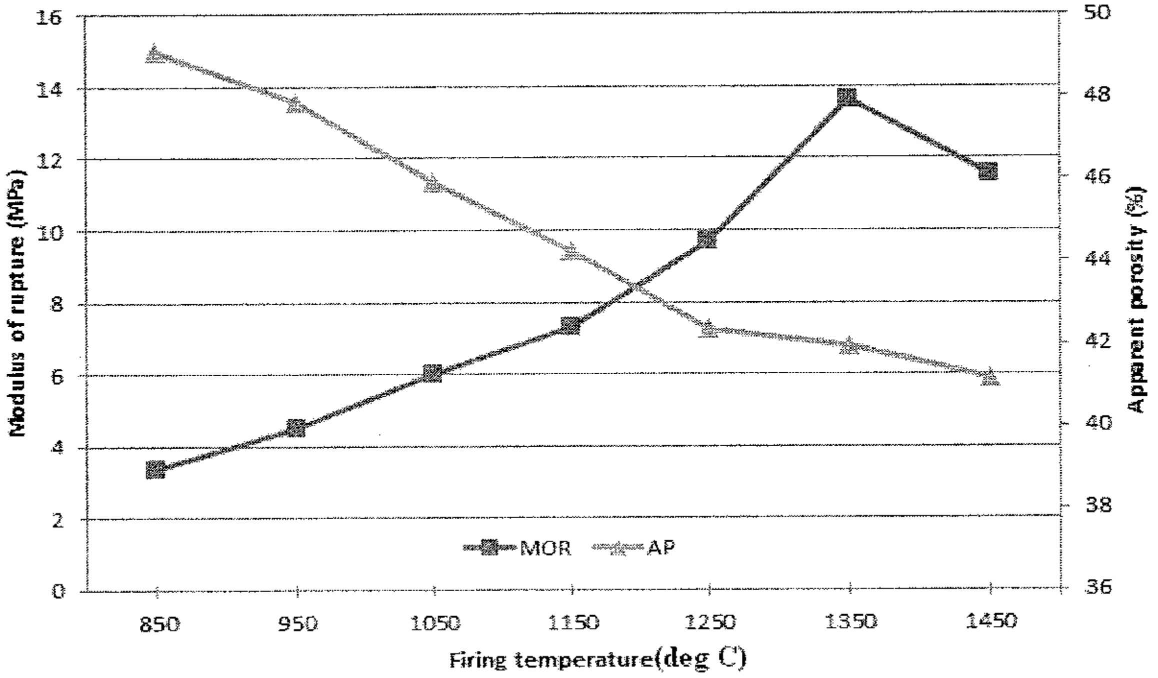


Figure 4.18: Effects of firing temperature on the MOR and percentage apparent porosity

4.3.4 Microstructure and Morphology of the Fired RHS Refractory

The subject of phase transformation and morphology are deep ones and require treatments at such depths, especially for newly developed refractories like has been done here. Such in-depth treatments, including thermal expansion studies with correlation with phase transformation are presented in section 4.4.

Figures 4.19 ((a) and (b)) show the effect of mineralizer concentration on the morphology of the sintered refractories. In the undoped refractory (Figure 4.19 (a)), only opaline silica is formed while the addition of slaked lime led to the formation of calcium silicate (a form of wollastonite). Beyond 2.6 wt. % of the slaked lime addition, pseudo-wollastonite is formed.

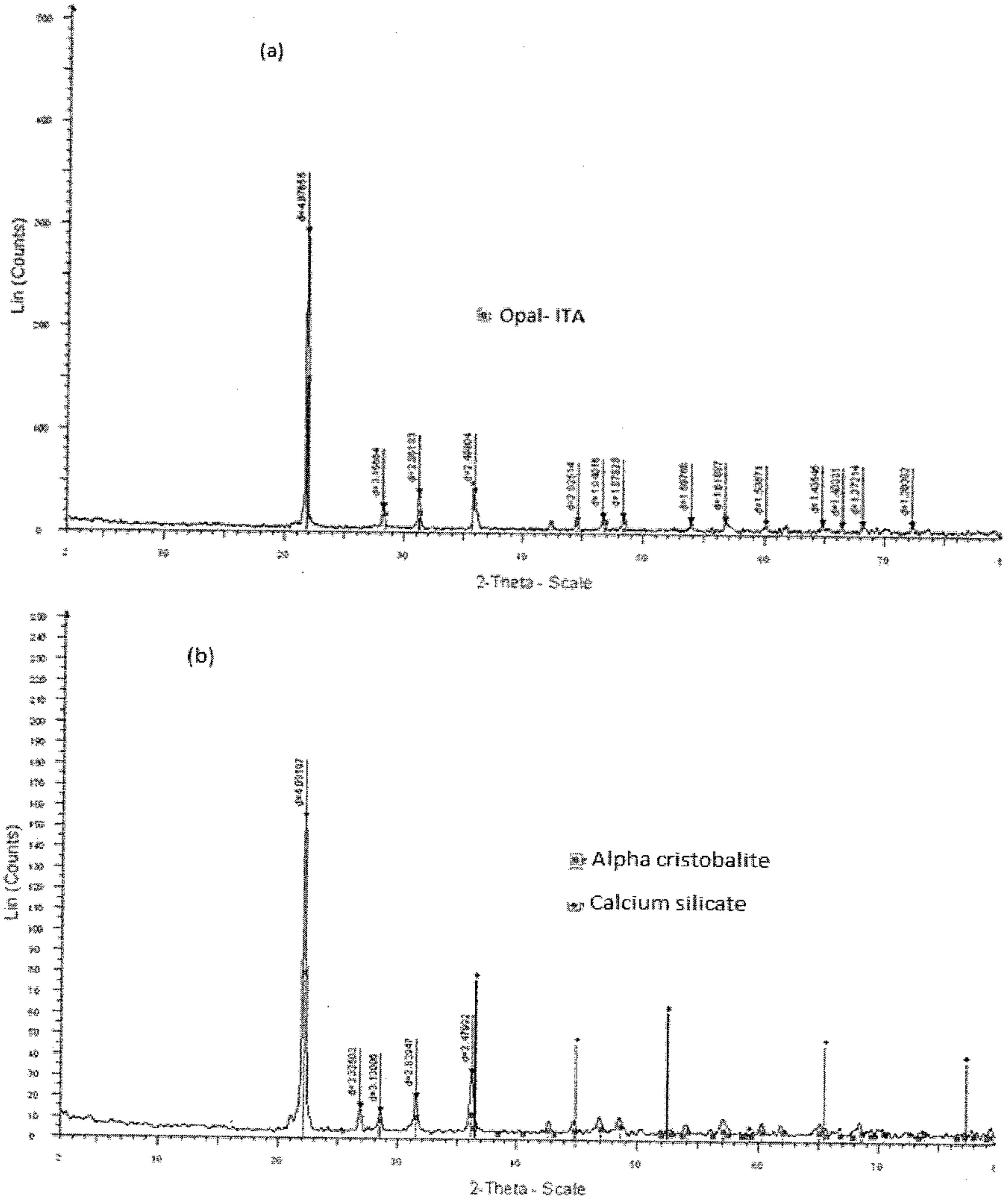
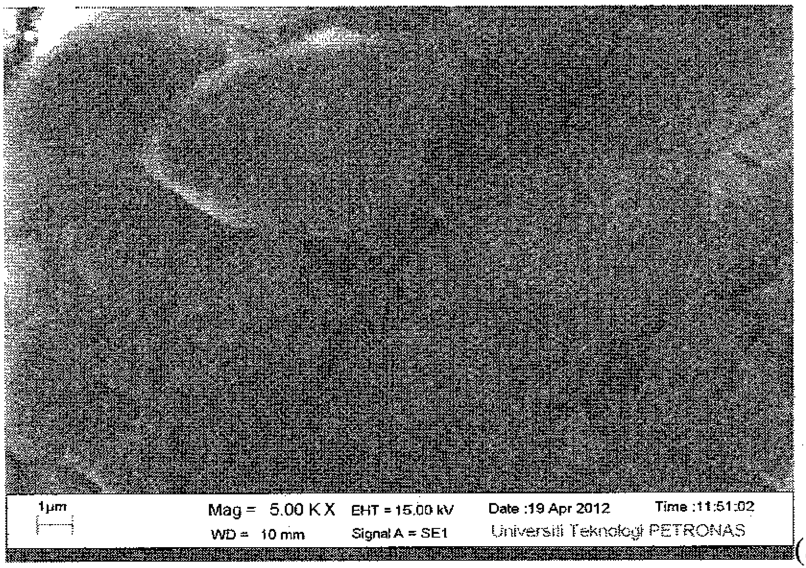
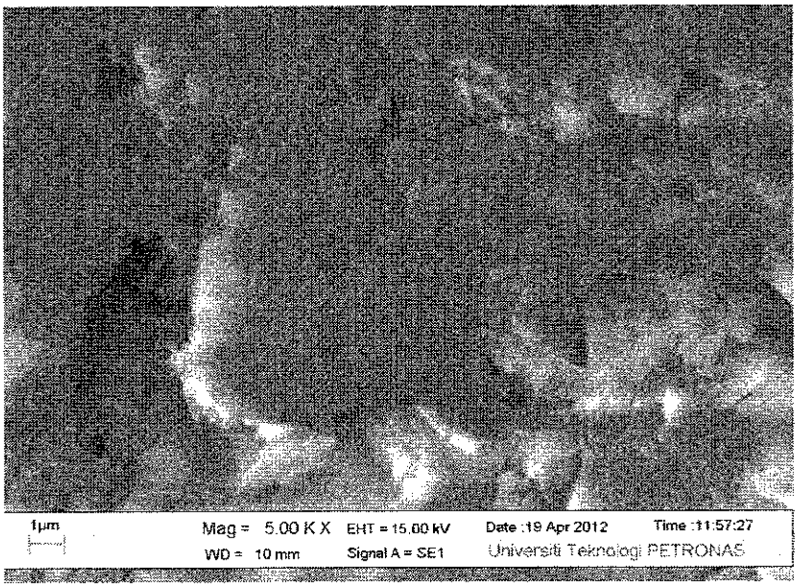


Figure 4.19: X-ray diffraction pattern of sample: (a) No mineralizer (b) 1.4 wt. % Mineralizer

There seems to be a relationship between firing temperature, densification and residual mineralogy of the refractories. As firing temperature increased, phase transformation occurred. At 850°C, the refractory is completely amorphous with many micro-cracks within the body as evidenced in Figure 4.20 (a). At 950°C, a vitreous glassy phase begins to appear. This vitreous phase increases up to 1050°C, when quartz and tridymite are remarkably noticed in the refractory (Figure 4.20 (c)). The quartz is effectively transformed completely to tridymite as at temperature range between 1150 and 1250°C, and wollastonite begins to appear thereafter. The coexistence of the tridymite and wollastonite gives way to cristoballite at about 1450°C, which then exists till melting point.



(a)



(b)

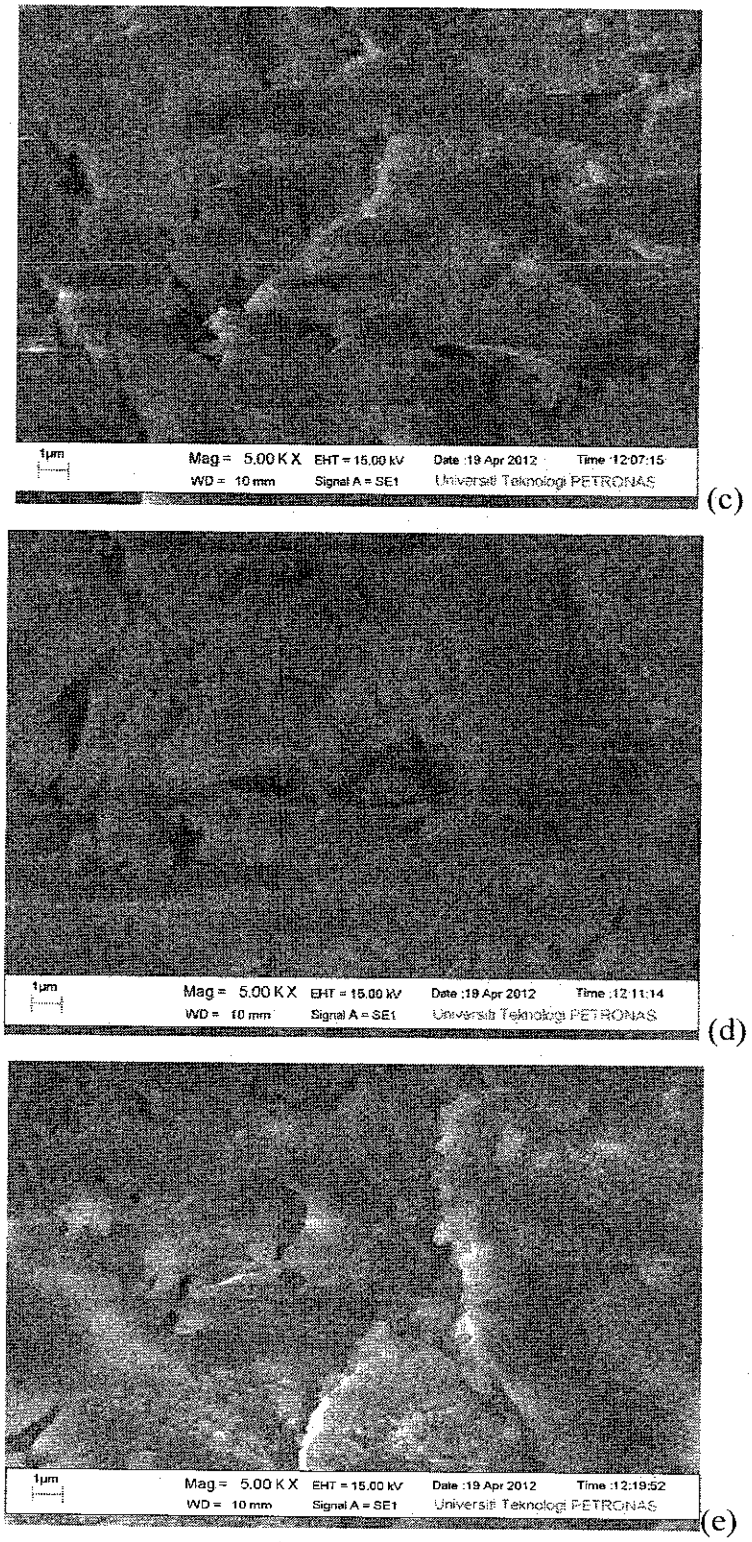


Figure 4.20: SEM images of fired RHS refractories at (a) 850°C and (b) 950°C (c) 1050°C (d) 1150°C (e) 1350°C

4.4 Thermal Expansion Behavior, Phase Transitions and some Physico-Mechanical Characteristics of Fired Doped RHS Refractory

4.4.1 Phase Transitions and Thermal Expansion Studies

The first section of this section discusses the phase transitions that occurred as the RHS refractory were fired from 850 to 1450°C. It is then followed by the thermal expansion behavior studies of the RHS refractory between the temperatures of 25 and 1500°C.

4.4.1.1 Phase Transitions in RHS Refractory

Figure 4.21 shows the x-ray diffractograms of the fired silica refractory. At 850°C, the refractory remains largely amorphous, dominated by opal-CT form of silica, referred to as silica glass by many authors [164].

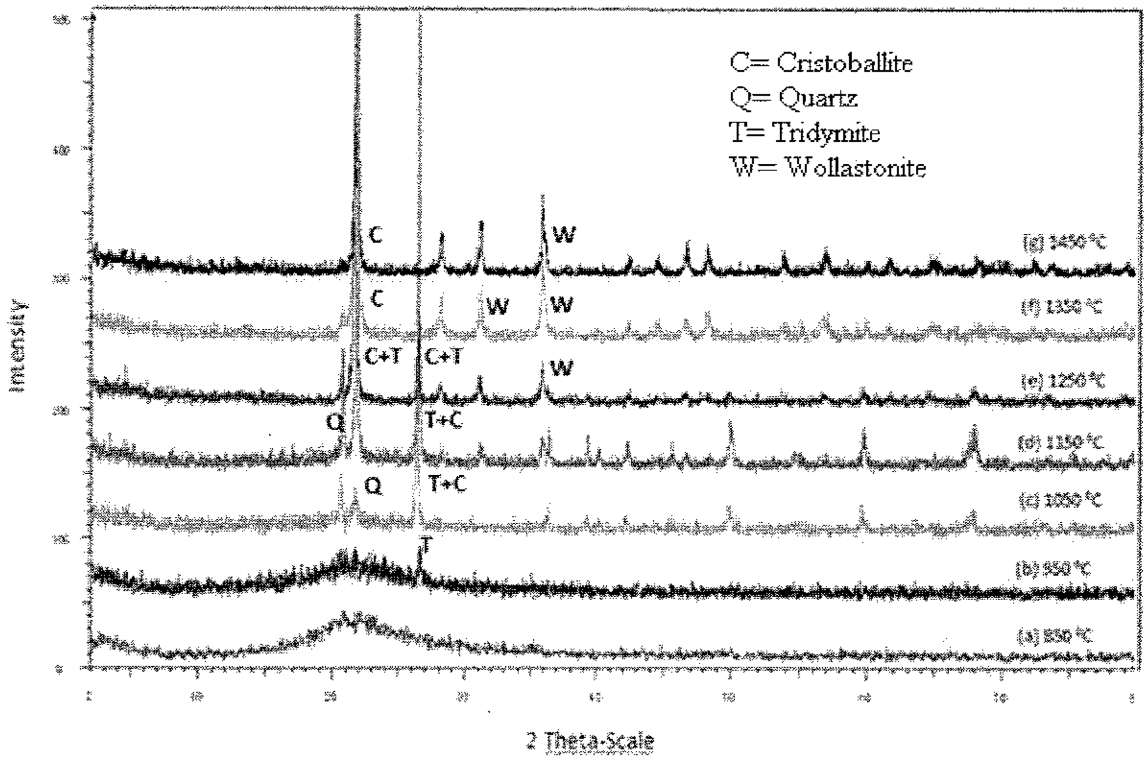


Figure 4.21: Stacked XRD patterns (a) - (e) of RHS refractory sintered at 850 to 1450°C

As the sintering temperature increases to 950°C, however, crystallization begins in the refractory body, with the formation of tridymite. This is the shoulder at $2\theta = 26.5^{\circ}$. However, the amorphous phase still remains the major phase in the entire refractory. At 1050°C, the entire refractory is now largely crystalline, with tridymite peaks at $2\theta = 22.5^{\circ}$ coexisting with a cristobalite phase growing strongly at $2\theta = 27^{\circ}$. At 1150°C, some of this cristobalite has inverted back to a hexagonal β-quartz and then forming a peak of cristobalite mixed with tridymite at $2\theta = 22.5^{\circ}$, 45° and 67.5°. At 1250°C, much of the tridymite had transformed to high temperature form of cristobalite, with traces of quartz. Also at this temperature, a wollastonite phase manifested at $2\theta = 36.5^{\circ}$and continues its growth progressively, becoming greatly pronounced at 1350°C. The quartz formed in addition to the tridymite still remaining have inverted completely to cristobalite between 1250 and 1350°C and so remained till 1450°C, which is the maximum temperature monitored for the transformation. At this temperature, the crystobalite coexisted with traces of wollastonite.

The early crystallization of the refractory at the temperature range between 850 and 1050°C is as a result of the dopant (mineralizer) - slaked lime and the OH^{-} group in opal, the presence of which lower the inversion temperatures of silica polymorphs [121, 164-168]. In fact, Nayak and Bera [164] have reported that complete crystallization of RHS of 99.87% purity only takes place at about 1300°C. The implications of these phase transitions for silica refractory performance are enormous.

Badly transformed silica bricks manifest considerable after-expansion effects during service temperatures, usually in excess of 1200°C. This is mostly as a result of the presence of high percentage of quartz, which exhibits high volumetric increase as it inverts to cristobalite beyond 1250°C. Thus, it is usually recommended [6] that depending on the grain size, residual quartz in silica refractory should range between 3 and 6 % for fine and coarse grains. As is evident from Figure 4.22, the after-expansion effect in the temperature range 1250 to 1350°C is not pronounced when considered in relation to the maximum witnessed at the range of temperature of 650 to 850°C. It is actually a negative expansion perceived to be a consequence of lattice contraction of tridymite.

4.4.1.2 Thermal Expansion Behaviour Studies of RHS Refractory

There are some salient inferences that could be deduced from the thermal expansion behavior of the doped silica refractory (Figure 4.23). In the temperature range of 25 to about 220°C, there is a gradual rise in the expansion of the silica refractory. The peak expansion in this temperature range is about 80 μm, or 0.24 % of the original 33.1 mm length of the fired silica refractory. At about 220°C, there is a sharp or sudden increase in the expansion from 80 μm to 230 μm or about 0.7 % (Table 4.7 refers) of the total fired length of 33.1 mm. This sharp expansion witnessed at 220°C is no doubt, a phase transition of a silica polymorph. From the reports of Kikuchi and Sudo [11], it represents the inversion of α- to β-cristobalite. This observation in the thermal expansion of RHS refractory is totally different from that of sintered silica refractory made from quartzite. In the quartzite manufactured silica refractory, there is a lack of this sharp rise at 220°C, instead, points of inflexion are noticed at temperature range of 117-163 or 570 - 580°C, corresponding to the inversions of low to high tridymite and α-quartz to β-quartz [16]. In the same vein, the magnitudes of the attendant expansion are different for RHS and quartzite refractories. While the normally reported linear expansion that accompanies α- to β-cristobalite is between 4-5 % for quartzite refractories on raw material basis [3, 169], it is lower for RHS refractory (0.7 %). The preliminary reason that could be adduced for this low expansion is the presence of the wollastonite phase in the sintered refractory, which acts as expansion stabilizer, inhibiting much of the expansion that would have occurred. One other effect the mineralizer exhibits is that it is able to undergo liquid phase sintering with many of the impurities in the RHS to form some visco-elastic phases. For instance, anorthite was detected in the sintered refractory. One of the positive effects of these visco-elastic phases is that they are capable of forming shields around crack-tips, thus leading to better thermal shock resistance [168].

From the curve of Figure 4.22, the maximum expansion witnessed (about 0.85 %) is found at the temperature range of between 650 to 850°C, and could be attributed to a combination of the volume expansions which characterize the transformation of α- to β-quartz and α- to β-cristobalite. After this expansion peak, the curve of the dilatogram shows a smooth and very low contraction in dimensions up to 1500 °C. In terms of thermal shock resistance, these observations hold good promise for low and high temperature thermal shock resistance. Apart from the sudden expansion at about 220°C, which is not high enough to cause macro cracks in the refractory body, the expanded volume is almost constant thereafter. This means the refractories would be able to cope with rapid changes in temperatures, whether at low or high temperature ranges. This assertion has been buttressed using Figure 4.23 and the explanations given alongside the figure.

It is interesting to note that these observed transitions from one polymorph to the other are reversible and this is clearly demonstrated in the lower of the cooling curves plotted in the dilatogram (Figure 4.22). The curves for the coefficients of thermal expansion, which gave peak values at 220°C are essentially for design purposes, which is not within the scope of the present work.

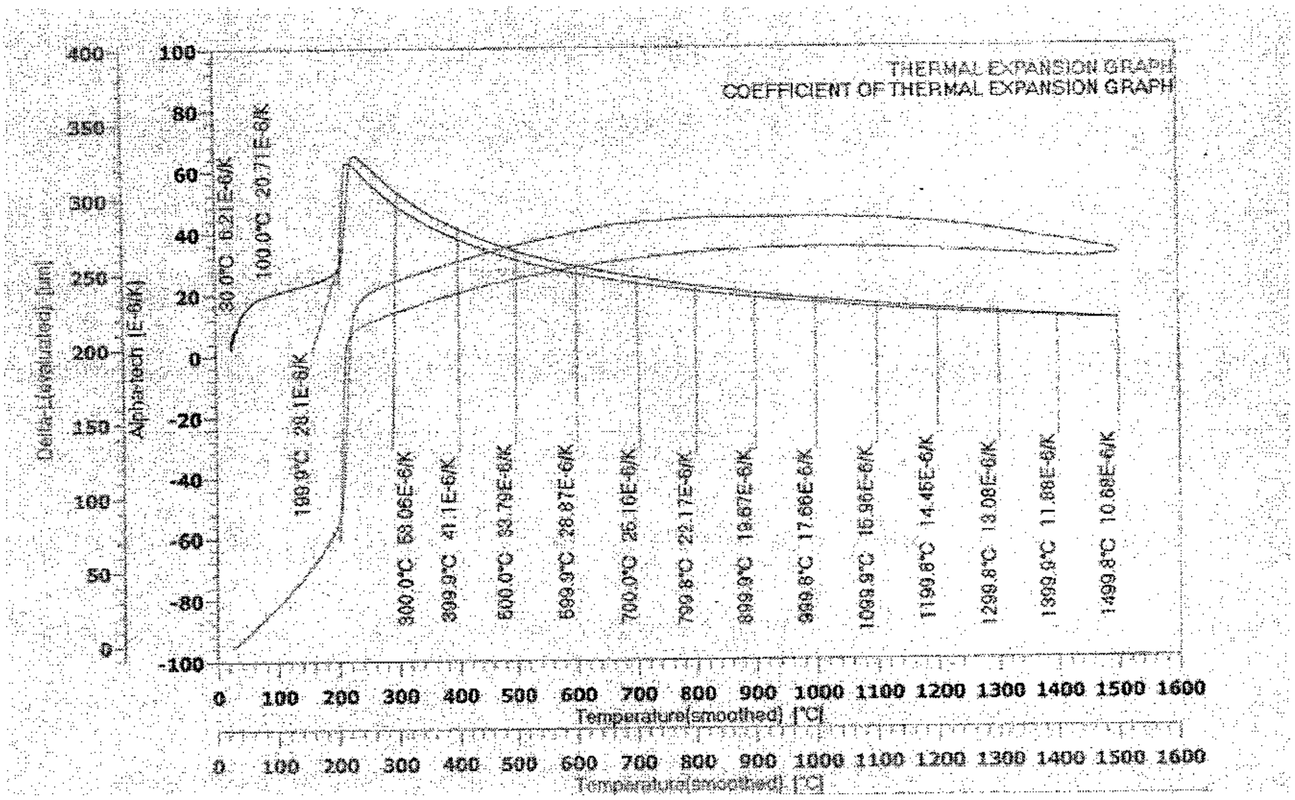
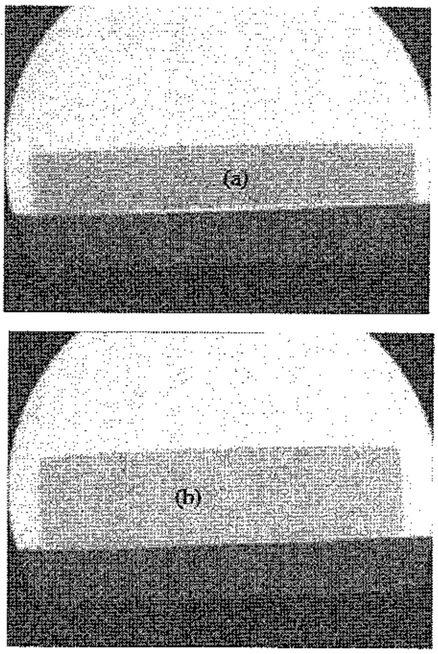
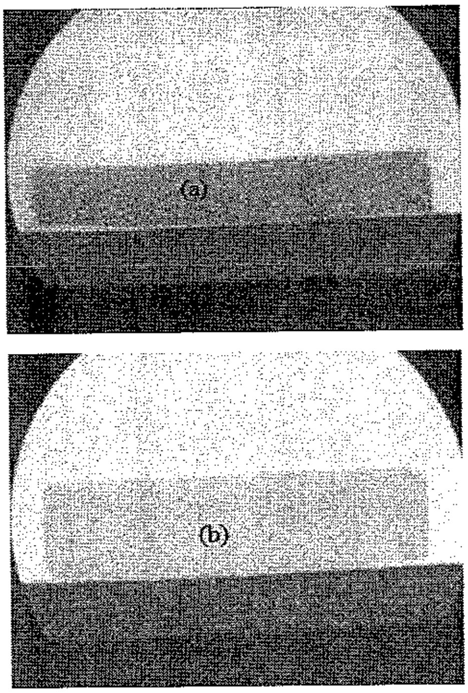


Figure 4.22: Graphs showing the curves of thermal expansion and coefficients of thermal expansion of the sintered refractory.

In order to prove the point of improved thermal shock resistance that was made above, samples of silica refractory were made, pre-fired at 1350 °C. The pre-fired samples were subjected to three thermal cycles within 25 and 650 °C using high heating rates 15, 20 and 25 °C/ min. X-ray radiographs were taken of the samples before and after the thermal cycles. Thereafter, the samples were observed for macro cracks formation. These were absent as evidenced in Figure 4.23. The traditional method for thermal shock resistance determination for silica refractory as prescribed by the BS 1902-1A [170] was employed. The samples were heated up to 450 °C and quenched in water and removed. At each point they were removed, the samples were observed for macro crack and if none was observed, they were pulled laterally by hand. They were placed right back in the furnace to be heated up again after observation. Five samples were tested and all of the samples withstood over 30 cycles before they could be pulled apart by hand. It is noteworthy that the recommended heating rate for silica refractory made from quartz sources in order to forestall the occurrence of macro crack formation is 10°C/ min [18].



(1)



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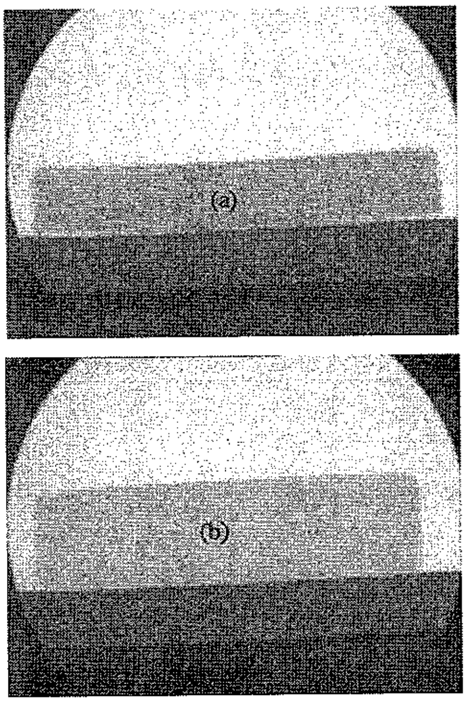

(3)

Figure 4.23: X-ray radiographs of RHS refractory samples (a) before and (b) after being subjected to high heating rates of (1) 15°/min (2) 20°/min and (3) 25°/min

4.4.2 Physico-mechanical Properties of the Produced RHS Refractory

Table 4.11 shows test results for the modulus of rupture (MOR), bulk density (BD), apparent porosity (AP), linear shrinkage (LS), permanent linear (reheat) change (PLC), linear thermal expansion (TE) and maximum linear thermal expansion (TE_{max}).

Table 4.11: Physico-mechanical properties of RHS, each quantity had sample size of five

Quantity	Mean Value	Standard deviation	Recommended or reported values
MOR (MPa)	13.93	0.0177	3.45 [146]
TE (%)	0.70	0.0148	4-5 % [3, 169]
TE_{max} (%)	0.85	0.0091	Up to 7 % [3]
BD (g/cm^3)	1.344	0.0044	0.72 to 0.76 [171]
AP (%)	41.92	0.0083	66 to 68 % [3]
LS (%)	5.40	0.0052	Not available
PLC (%)	0	0	Not available

In the MOR test, 5 samples were investigated. Figure 4.24 shows a representative load-extension obtained from the plotter of the 5kN UTM.

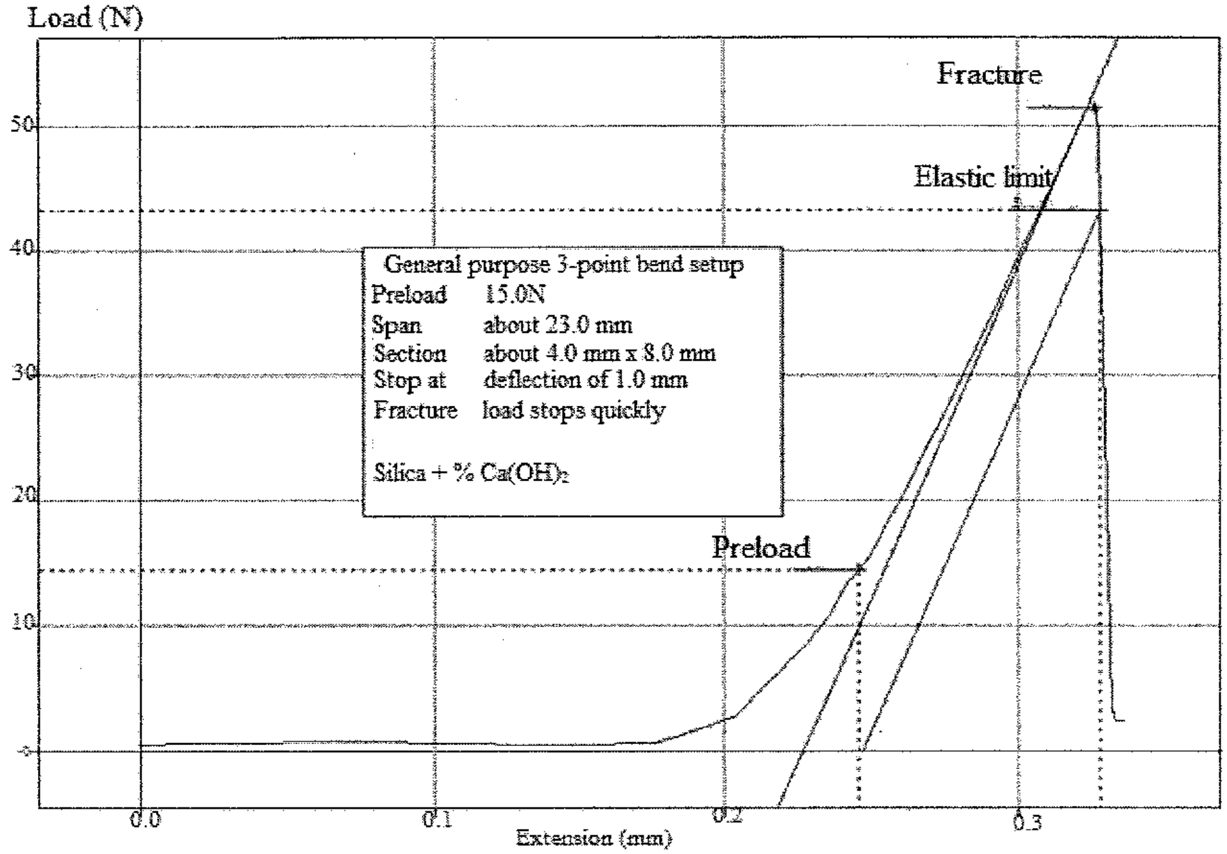

Figure 4.24: A typical load- extension diagram obtained from the UTM used for MOR tests

The ASTM C133 [144] prescribed equation for calculating MOR for a three-point bend test is:

$$MOR = \frac{3PL}{2bd^2} \tag{4.4}$$

In equation (4.4) L, b and d are respectively the span (distance between mid-pivot crests), the width and the thickness of the fired specimen, while P is the applied load. From Figure 4.24, the values of these parameters are clearly shown, obtained and used in the prescribed equation (4.4), to calculate the MOR. The results and the accompanying statistics (standard deviation) are presented in Table 4.11. The result shows a mean MOR of about 14 MPa and compared to the prescription of 3.45 MPa for silica refractory in ASTM C133 [144], it could be concluded that this MOR result is a positive indicator.

BD and AP share an inverse proportional relationship and they are useful in refractory for the purposes of the control of mechanical properties and thermal conductivity. Usually, the higher the AP, the lower the BD, thermal conductivity and MOR. Although there are no standard values prescribed for the bulk density or apparent porosity of silica refractory, literature [68] has reported that rice husk silica insulating refractory employing lime as dopant ranged between 0.72 to 0.76 g/cm^3 for BD and 66 to 68 % for AP. Comparing these values with the results of the current research as shown in Table 4.11, it is clear that this work reports superior values. The reason that could be adduced for these improved properties is that the process parameters (compaction pressure, firing temperature, and percentage of the dopant) for the production of silica refractory had been optimized (though not reported along this paper for want of space). Thus, the use of compaction pressure of 105 MPa, firing temperature of 1350°C and 1.4 wt. % of the mineralizer are not just arbitrary.

Using the optimized production parameters stated above, the RHS refractory recorded a zero percent reheat change, which was performed in accordance with ASTM C113 [148]. This is due to the stabilization effect of *wollastonite* and the very low, but reversible thermal expansion of the refractory. The linear shrinkage is about 5.4 %, which may be due to a combination of loss on ignition, liquid phase sintering and lattice contraction.

4.4.3 Refractoriness

Refractoriness of a ceramic or refractory is the highest temperature the material can withstand before it begins to fuse. It is an indicator used to obtain some information of what the operating temperature of the ceramic or refractory could be. In this test, the effect of the dopant on the refractoriness of the RHS refractory was in studied. Samples A, B, C, D and E respectively contained 0, 1, 1.4, 1.8 and 3.4 wt.% of the slaked lime. As evident from Figure 4.25 (b), the mix containing between 1 and 1.8 wt.% of slaked lime witnessed negligible distortions. All samples withstood a firing temperature of 1650°C (which corresponds to standard Cone number 28) without melting, but the distortions in samples A and E suggest that their mix (0 and 3.4 wt. %

of slaked lime respectively) may not be suitable for RHS refractory manufacture. This is because such distortions could result in refractory brick warpage while in use.

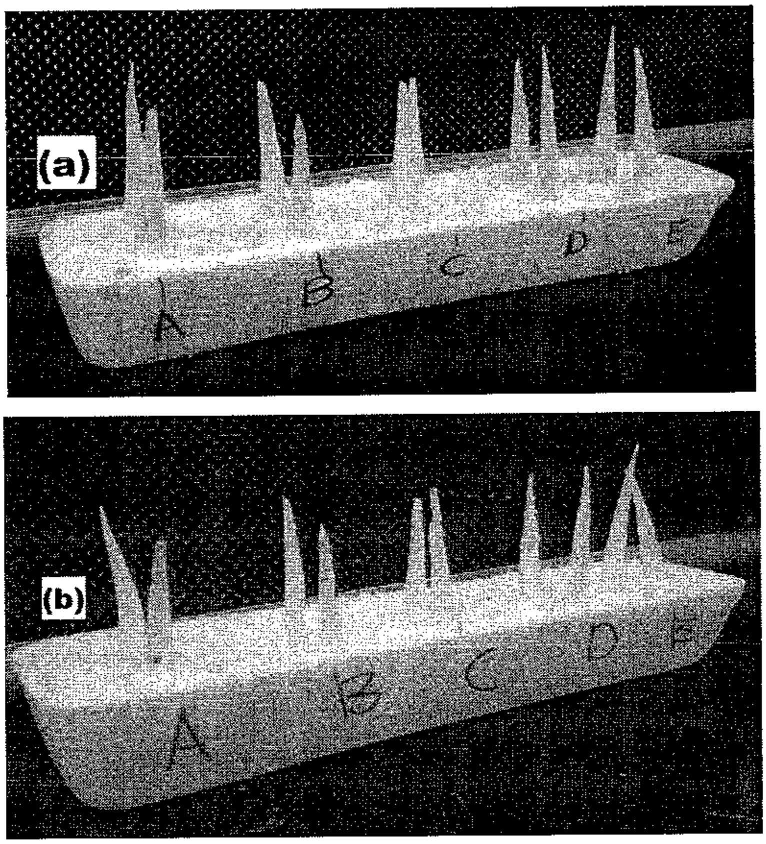

Figure 4.25: PCE cones of RHS refractories: (a) before and (b) after firing at 1650°C.

4.5 Chapter summary

This chapter has presented and discussed the results obtained from this research. The chapter is organized into three sections according to the research objectives outlined in section 1.4. Section 4.2 presented the findings on the development of the HTB process for the production of high purity RHS, with the production process parameters fully optimized and the product characteristics well established.

In section 4.3, production of RHS refractory was presented. The production process parameters were optimized while the characteristics of the RHS refractory produced were discussed.

Results for the thermal expansion behavior and phase transitions occurring in RHS refractory were presented in section 4.4, thus concluding the aim of the research.

The results of the HTB process have shown that the newly developed process is faster than other processes it was compared with, having obtained over 99% pure RHS. The optimal values of process factors were established too. In the same vein, investigations on the produced RHS refractory indicated that they have good thermal shock resistance, having withstood heating rates of 25°C per minute as contrasted to the 10°C per hour that quartzite silica refractory can withstand, without cracking.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Chapter Overview

This chapter summarizes the major findings of this research. Section 5.2 presents the major conclusions on the three objectives that this research set out to investigate. This is followed by the contributions of the research presented in section 5.3. The chapter ends with recommendations for future research, which are presented in section 5.4.

5.2 Conclusion

The aim of this research, which is: to develop and optimize a process that is fast for the production of high purity silica from rice husk, as well as apply the silica produced from the process to carry out optimized laboratory scale manufacture of hot-face, stand-alone silica refractory, has been accomplished. The three specific objectives were deeply researched with outcomes summarized as follows.

5.2.1.1 The Hydro Thermo-baric Process

A novel method- the hydro thermo-baric process was developed and used to produce high purity silica from rice husk. The factors that influence the HTB process were identified as water to husk ratio (WTHR), temperature (TEMP) and soaking time (SOKT). These process factors were optimized through a combination of the OVAT method and the method of factorial design of experiments. The optimized values were: WTHR- 6.98g/ml; TEMP- 286.13°C and SOKT- 15.68 minutes. The produced submicron size (117nm) RHS were characterized using XRF, XRD, FESEM and

EDX. XRD results show that the silica produced is amorphous in nature. The purity level obtained (approximately 99%) with this process route was comparable to that obtained with the hydrochloric acid leaching method. The product purity level obtained could be useful in adsorbent, refractory, silicon carbide and zeolite production applications. FESEM images and particle size analysis showed that the particles have submicron (117 nm on the average) size. However, EDX results show an increase in residual carbon in the silica, with increase in the soaking time. This implies that depending on application needed, the process parameters could be varied to obtain silica with various degree of residual carbon. The process yield was determined to be 92.5% on average and is adjudged to be able to support needs of the refractory industry. Compared with the sol-gel or acid leaching methods of RHS production, HTB process was the fastest, being able to produce RHS of over 99% in only 30 minutes. Other processes take up to14 hours processing time.

5.2.1.2 Thermal Expansion Behavior, Phase Transitions and Properties of RHS Refractory

The thermal expansion behaviour of slaked lime doped rice husk silica (RHS) refractory was investigated between 25 to 1500°C. Also, phase transition analysis within the temperature range of 850 to 1450°C at interval of 100°C was studied. A sudden expansion of 0.7% noticed at 220°C is due to the transformation of α- to β-cristobalite. The highest expansion (0.85%) reached within the temperature range of 650 to 850°C, remained almost constant for the investigated temperature range, and was not high enough to cause macro cracks in the refractory. From the work it is evident that RHS silica refractories only have a sharp, but low thermal expansion (0.7%) at a temperature of about 220°C, which is considered not high enough to cause macro cracks in the refractory body. This conclusion was bolstered by the fact that the employment of high heating rates (25°C per minute) could not cause the RHS refractory to crack, as revealed by the x-ray radiographs. Thus, it is inferred that RHS refractory has better low temperature thermal shock resistance than silica refractory made from quartzite, since quartzite made silica refractory would crack when heating rates of more than 10°C per hour are employed. The phase transitions witnessed in the temperature range between 850 and 1450°C are similar to those of quartzite silica refractories, though the crystallization temperature was lowered due to the presence of the dopant.

The MOR observed for these refractories is about 14MPa (Table 4.11), which is approximately four-fold (3.45MPa) of the recommended value for silica refractory. The moderate values of apparent porosity and bulk density of the investigated RHS refractory coupled with the high refractoriness (in excess of 1650°C) make them suitable for application in coke ovens, without the risk of low temperature thermal shock resistance that is associated with quartzite manufactured silica refractory.

5.2.1.3 Optimized Production Parameters of RHS Refractory

The parameters necessary to aid the industrial production of rice husk silica refractory using PEG 8000 as binder and slaked lime as dopant (mineralizer) have been studied. The optimal value of the dopant - $Ca(OH)_2$ was determined to be around 1.4%. Since silica refractory have very fragile green form, it is required that shapes made from RHS refractory be pre-fired. The investigations carried out have shown that an optimum pre-firing temperature should be chosen from the range of 1250 to 1350°C, since the highest MOR necessary for handling occurs within this range. This increase in strength is linked to the formation of highest tridymitization of the refractory body in this temperature range. The compaction pressure range that is optimal for good fired density, apparent porosity and MOR falls between 90 and 110 MPa.

5.3 Research Contributions

1. The research has developed a new process for the production of RHS, faster than the existing methods.
2. This research has provided insight into the thermal expansion behaviour of RHS refractory, which is hitherto unknown in literature or in the refractory industry. It has clearly shown that RHS refractory possesses one inversion point- the transformation which takes place at about 220°C, unlike the silica

refractory made from quartzite that has three distinct inversion temperatures. The research has shown that the value of the sudden expansion in RHS refractory is much lower than that of made from the traditional sources and hence can withstand rapid firing regime, which is impossible with the traditional silica refractory.

3. The research has laid the foundation for silica refractory manufacture using rice husk, by laying out the values of the production process parameters. This information is hitherto unavailable in literature. And to aid the derivation of RHS to support this industry, this research has developed a new production route called the hydro thermo-baric process. The versatility of the process could be of help in obtaining RHS of various degrees of purity, depending on the application for which the RHS is intended for use. This various purity levels are made possible by adjusting any of the process parameters.

5.4 Recommendations

1. It was stated in section 4.1.5 that products obtained from the hydro thermo-baric process contained only negligible traces of metallic impurities, with amorphous structure and submicron particle size, though the product has some residual carbon adsorbed on to its surface. The purity level obtained with this process route was comparable to that obtained with the hydrochloric acid leaching method. The product purity level obtained could be useful in adsorbent, refractory, silicon carbide and zeolite production applications. Further research is proposed to fully understand the chemical reaction kinetics that accompany the process taking place in the reactor.
2. The service related properties of this refractory, such as the refractoriness under load, creep in compression, hot modulus of rupture or thermal conductivity at elevated temperature have not been determined due to dearth of specialized equipment needed to carry out such tests. Collaboration with ceramic research centres could be made and is hereby recommended, so that such characterization is fully carried out. Further investigations into the factors

that affect the BD- compaction pressure relationship are recommended. Also, a scale-up of the HTB process is recommended.

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APPENDIX A

LIST OF PUBLICATIONS

(1) Ugheoke B. I,. O. Mamat and Bambang A. W. A Brief Survey of the Literature on Silica Refractory Research and Development: the Case for Nanostructured Silica Obtained from Rice Husk Ash (RHA). Defect and Diffusion Forum Vol. 307 (2010) pp 53-62.

(2) Ugheoke, B. I. and Mamat, O. Hydro thermo-baric processing and properties of nano silica from rice husk, Applied Mechanics and Materials Vols. 152-154 (2012), pp. 177-182.

(3) Ugheoke B.I. and O. Mamat. A Novel method for high volume production of nano silica from rice husk: process development and product characteristics, IJMatEI, Volume 3 No. 2 (2012), pp. 139-155.

(4) Ugheoke B.I. and O. Mamat. A critical assessment and new research directions of rice husk silica processing methods and properties, Maejo Int. J. Sci. Technol. 2012, 6(03), 430-448.

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(6) B. I. Ugheoke, O. Mamat and B. Ari-Wahjoedi. Optimization of production process parameters of rice husk silica (RHS) refractories, Journal of the Australian Ceramic Society Volume 49 [1], 2013, 98 – 106.

(7) B. I. Ugheoke, O. Mamat and B. Ari-Wahjoedi. Notes on the thermal expansion behaviour, phase transitions and some physico-mechanical characteristics of fired doped rice husk silica refractory, Journal of Advanced Ceramics, Volume 2, Issue 1, 2013, pp 79-86.