

**COST-EFFECTIVE SYNTHESIS OF HIGH PURITY
PRECIPITATED SILICA FROM LOCALLY AVAILABLE RICE
HUSK ASH**

by

Mahmudul Islam Tapu

MASTER OF SCIENCE IN
GLASS AND CERAMIC ENGINEERING


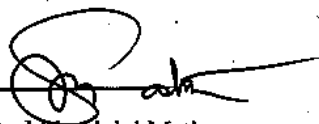
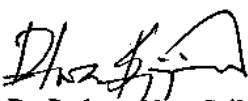



Department of Glass and Ceramic Engineering
BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY
DHAKA, BANGLADESH

June, 2018

The thesis titled “Cost-Effective Synthesis of High Purity Precipitated Silica from Locally Available Rice Husk Ash” submitted by Mahmudul Islam Tapu, Roll No.: 0412172002, Session: April, 2012 has been accepted as satisfactory in partial fulfillment of the requirement for the degree of Master of Science in Glass and Ceramic Engineering on 27 June 2018.

BOARD OF EXAMINARS

- 
1. Dr. Muhammad Hasanuzzaman
Assistant Professor
Department of Glass and Ceramic
Engineering, BUET, Dhaka-1000
Chairman
(Supervisor)
- 
2. Dr. Md. Abdul Matin
Associate Professor and Head
Department of Glass and Ceramic
Engineering, BUET, Dhaka-1000
Member
(Ex- officio)
- 
3. Dr. Redwan Noor Sajjad
Assistant Professor
Department of Glass and Ceramic
Engineering, BUET, Dhaka-1000
Member
- 
4. Mr. Arman Hussain
Assistant Professor
Department of Glass and Ceramic
Engineering, BUET, Dhaka-1000
Member
- M. HASAN

5. Dr. Mahbub Hasan
Associate Professor
Department of Materials & Metallurgical
Engineering, BUET, Dhaka-1000
Member
(External)

CANDIDATES' DECLARATION

It is hereby declared that except where specified by reference to other works, the studies embodied in this thesis are the results of investigation carried out by the author under the supervision of Dr. Muhammad Hasanuzzaman, Assistant Professor, Department of Glass and Ceramic Engineering, BUET. Neither the thesis nor any part of it has been submitted elsewhere for any other purposes.



(Mahmudul Islam Tapu)

Student ID: 0412172002

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and the Most Merciful

It has been a long journey to finish my post-graduation. I could have never been able to be where I am and who I am without the help of Almighty **Allah**.

I would like to express my greatest gratitude and indebtedness to my supervisor Assistant Professor **Dr. Muhammad Hasanuzzaman** for providing the opportunity to complete my master's thesis under his exceptional guidance. Without his untiring patience, constant encouragement, guidance, and knowledge this work would not have been possible. I appreciate for providing me the intellectual freedom of work on research work. I admire his profound knowledge, experience, and enthusiasm in research. His excellence of understanding experimental results inspires me.

I express my sincerest acknowledgement to my course advisor **Dr. M.A. Matin** for his constructive guidance, generous support and inspired suggestions during the period and also express my deepest gratitude to **Dr. A.K.M. Hakim, Dr. Md. Fakhru Islam, Dr. Redwan Noor Sajjad** and **Mr. Arman Hussain** for their caring, inspiration, helpful guidance and encouragement.

I would like to thank CASR for extending my period of post-graduation to carry out this research work and grateful to my thesis board members for their valuable suggestions and for reviewing my dissertation and also thanks to all the staffs of the department of GCE and my dearest batch mates.

I express my deepest gratitude to my family for all their love, support, and encouragement throughout my life to this point. Without their encouragement this work would not have been possible. I especially want to thank my parents Nazrul Islam and Nargis Sultana, my brother and sister, in-laws for their many sacrifices and supports for us.

Last but not least, I would like to thank my spouse Samia Sharif for her love, unwavering support, patience and companion through many ups and downs. I owe this thesis to our little beloved 2.5-year-old son, Shehzad Islam for bringing the happiness to my family every day. They all truly share in this accomplishment.

ABSTRACT

Revolutionary bio-material Rice Husk Ash (RHA) has high potential to help the tire and rubber industry to become more sustainable. This material has also a good candidate to reduce energy consumption and CO₂ emission. The conventional process of manufacturing precipitated silica by sand fusion with soda ash followed by acidification, is highly energy intensive and expensive as the process requires the reactants to be heated to high temperatures of around 1400°C. The rising cost of raw materials such as sodium silicate, soda ash and fuel in international market is also the reason to seek the alternative manufacturing route of silica production. In contrast, rice husk ash, an environmental burden made by burning rice husk (RH) as fuel to generate thermal energy, would be an important and potential alternative cheaper silica source for producing silica where the silica content can be as high as 97%. In this study, a cost-effective synthesis method of commercial grade precipitated silica ($\geq 99\%$) has been developed based on alkaline extraction method of silica from locally available rice husk ash.

An integrated process flow sheet was developed and practiced that included initial leaching, alkali extraction of rice husk ash, acid precipitation of sodium silicate and finally drying and pulverizing of as produced precipitated silica from rice husk ash. Alkali extraction of purified rice husk ash was investigated within the temperature range of 120-170°C. The extracted sodium silicate solution was then acidified by sulphuric acid to reduce pH of the solution to ~ 7 . At around pH 7, precipitation process of silica was completed. After washed, precipitated silica was aged, dried and pulverized to get fine powder. Analysis of rice husk ash and final precipitated silica powder by X-Ray Fluorescence (XRF) showed amorphous silica content 88-97% and 97-98% respectively. X-ray diffraction results confirmed presence of amorphous silica due to the broad peak zone and presence of trace amount crystalline silica due to the presence of cristobalite. The effects of temperature, pH, leaching agents, acid concentrations, alkali and acid amount optimized in this study.

A production cost analysis was also carried out, which shows the developed synthesis route of high purity precipitated silica from rice husk ash cost ~ 43 BDT/kg. Whereas, other existing commercial process cost >46 BDT/kg for producing precipitated silica, which indicates the suitability and exploitability of the cost-effective synthesis process being developed in this research work for producing high purity precipitated silica.

TABLE OF CONTENTS

ACKNOWLEDGEMENT.....	iv
ABSTRACT.....	v
TABLE OF CONTENTS.....	vi
LIST OF FIGURES	ix
LIST OF TABLES	xi
LIST OF ABBREVIATIONS	xii
1. INTRODUCTION	2
1.1 Background of the Research.....	2
1.2 Problem Statement.....	4
1.3 Objectives of the Research	4
1.4 Outline of the Thesis	5
2. LITERATURE REVIEW	8
2.1 Silicon Dioxide.....	8
2.1.1 Molecular structure of silicon dioxide	9
2.1.2 Physical properties of silicon dioxide	11
2.1.3 Chemical properties of silicon dioxide	11
2.1.4 Solubility of silica in water.....	14
2.1.5 Uses of silicon dioxide	14
2.2 Silicon Dioxide – Amorphous Form	15
2.2.1 Physicochemical properties of precipitated silica	17
2.2.2 Manufacturing process of precipitated silica from silica source	18
2.3 Demand of Precipitated Silica in Various Market.....	24
2.3.1 Precipitated silica market worth 2.23 billion USD by 2021	24
2.3.2 Analysis of imports of precipitated silica from India to Bangladesh.....	25
2.4 Industrial Application of Precipitated silica.....	26
2.4.1 Non-rubber grade precipitated silica	26
2.4.2 Rubber grade precipitated silica.....	27
3. EXPERIMENTAL METHODOLOGY	34
3.1 Introduction	34
3.2 Schematic Representation of Research Work	35
3.3 Rice husk ash (RHA).....	36

3.4	Other Chemicals.....	37
3.4.1	Commercial grade caustic soda flakes (NaOH).....	37
3.4.2	Commercial grade hydrochloric acid (HCl).....	38
3.4.3	Commercial grade sulphuric acid (H ₂ SO ₄).....	38
3.5	Chemical Reagents	38
3.6	Equipment and Instrument.....	38
3.7	Characterization Techniques	39
3.8	Experimental Methods	39
3.8.1	Alkaline extraction of rice husk ash	40
3.8.2	Precipitation of silica.....	40
3.9	Characterization of Rice Husk Ash by Analytical Methods	40
3.9.1	Determination of moisture content of rice husk ash	41
3.9.2	Determination of silica content present in rice husk ash	41
3.9.3	Determination of residual carbon content in rice husk ash through loss on ignition.....	42
3.10	Removal of Metal Impurities by Acid Leaching	43
3.10.1	Extraction of silica by alkaline extraction of rice husk ash.....	44
3.11	Analytical Methods of Checking the Properties of Alkaline Silicate	46
3.11.1	Specific Gravity of alkaline silicate solution	46
3.11.2	Soluble silicate content of diluted alkaline silicate solution	47
3.11.3	Alkalinity of alkaline silicate solution	48
3.11.4	Silica content of alkaline silicate solution	48
3.11.5	Molar Ratio of soluble silica to alkali	48
3.12	Precipitation of Silica from Sodium Silicate.....	48
3.12.1	Preparation of sulphuric acid solution.....	49
3.12.2	Preparation of sodium silicate solution.....	49
3.12.3	Acidification of alkaline silicate solution.....	50
3.12.4	Separation of precipitated silica by vacuum filtration	50
3.12.5	Purification of precipitated silica by removing sodium sulphate	51
3.12.6	Aging and Drying	51
3.12.7	Pulverizing.....	52
3.12.8	Associated recoveries	52
3.13	Analytical Methods for Checking the Quality of Precipitated Silica.....	52
3.13.1	Determination of purity of precipitated silica	52

3.13.2	Specific gravity of sodium silicate solution	53
3.13.3	Presence of chlorides.....	53
3.13.4	Presence of sulphates.....	54
3.13.5	Determination of pH.....	54
3.13.6	Moisture content	55
3.13.7	Loss on Ignition (LOI)	55
3.13.8	Bulk density	55
3.13.9	Determination of size distribution of particles through sieve analysis	55
3.14	Summary of Characterization of Raw Materials and Products.....	56
3.14.1	Characterization of rice husk ash.....	56
3.14.2	Characterization of products from different stage	56
3.14.3	Characterization techniques.....	57
4.	RESULTS AND DISCUSSION.....	65
4.1	Characterization of As-received Rice Husk Ash (RHA).....	65
4.1.1	Optical image of rice husk ash (as-received)	65
4.1.2	Chemical composition analysis of rice husk ash	66
4.1.3	Reactive amorphous silica content and moisture content of rice husk ash	67
4.1.4	Phase analysis of rice husk ash	68
4.1.5	Morphological properties of rice husk ash	69
4.2	Purification of As-received Rice Husk Ash (RHA).....	70
4.2.1	Effect of leaching treatment	71
4.3	Quantitative Results of the Experiments Conducted in this Research.....	74
4.4	Characterization of Products Obtained from Different Stages of Experiments	77
4.5	Influence of Different Reaction Variables to Prepare High Purity Precipitated Silica.....	79
4.5.1	Effect of pH and silicate content.....	79
4.5.2	Gelation time	81
4.5.3	Syneresis	83
4.6	Characterization of As- produced Precipitated Silica	86
5.	PRODUCTION COST ANALYSIS.....	92
6.	SUMMARY, CONCLUSIONS AND FUTURE WORK	94
6.1	Summary and Conclusions	94
6.2	Future Work.....	95
REFERENCES.....		96

LIST OF FIGURES

Fig. 2.1 (a) Optical image of crystalline and amorphous silica; (b) Structure of crystalline silica; (c) Structure of amorphous silica	9
Fig. 2.2 (a) Structure of fused silica glass along with; (b) a six-membered ring structure of SiO ₂	10
Fig.2.3 Typical XRD pattern of amorphous silica from RHA	15
Fig. 2.4 Structure of Precipitated Silica	16
Fig. 2.5 Basic flow diagram of producing sodium silicate by Furnace route.	19
Fig. 2.6 Basic flow diagram of producing sodium silicate by hydrothermal route.....	19
Fig. 2.7 Global precipitated silica market by geography	24
Fig. 2.8 U.S Precipitated Silica market revenue, by application, 2012 - 2022 (USD Million)	25
Fig.2.9 Total quantity and value of imports of precipitated silica 2014 – 2016	26
Fig. 2.10 Different uses of precipitated silica as adhesive.....	28
Fig. 2.11 Precipitated silica is used in all types of rubber soled footwear.....	28
Fig. 2.12 Precipitated silica is used to improve strength of rubber belts	29
Fig. 2.13 Precipitated silica is used to improve pigment dispersion and acts as a pairing agent in PVC sheets	29
Fig. 2.14 Precipitated silica is used to increase abrasion properties and durability of railway pads	30
Fig. 2.15 Rice rollers and Rubber rollers	30
Fig. 2.16 Rubber products and rubber hoses.....	31
Fig. 2.17 Silicon Tubes	32
Fig. 2.18 Rubber and solid tires	32
Fig. 2.19 Textile Cots and Aprons	32
Fig. 3.1 Schematic diagram of research work.....	35
Fig. 3.2 Rice husk ash as-received collected from various rice mills.....	37
Fig. 3.3 Determination of silica content in rice husk ash.....	42
Fig. 3.4 The set-up for acid leaching treatment of rice husk ash	44
Fig. 3.5 Alkali extraction in laboratory glass beaker and in pilot digester	45
Fig. 3.6 Separation of carbon residue by filtration in Lab.	46
Fig. 3.7 Hydrometer.....	47
Fig. 3.8 Density was tested by deeping the hydrometer in the liquid.....	47

Fig. 3.9 Nickel crucible in muffle furnace	47
Fig. 3.10 Acidification of alkaline solution	50
Fig. 3.11 (a) Separation of silica by filtration; (b)Wet precipitated silica after filtration	51
Fig. 3.12 (a) Formation of transparent gel solution; (b)Transparent solid gel after filtration.....	51
Fig. 3.13 Precipitated silica powder after drying and milling.....	52
Fig. 3.14 Schematic diagram of X-ray fluorescence.....	59
Fig. 3.15 (a) XRF machine used in this research (b) Tablet preparation for XRF test...	59
Fig. 3.16 X-Ray Diffraction (XRD) machine	60
Fig.3.17 Field Emission Scanning Electron Microscope (FESEM)	62
Fig. 4.1 Optical images of rice husk ash.	65
Fig. 4.2 XRD result of as-received rice husk ash.....	69
Fig. 4.3 SEM micrograph of rice husk ash (as-received) (a) SEM image of rice husk ash (1 μm ; x 10,000); (b) SEM image of rice husk ash (1 μm ; x 10,000); (c) SEM image of rice husk ash (100 nm; x 30,000); (d) SEM image of rice husk ash (100 nm; x 30,000)	70
Fig. 4.4 Effect of HCl concentration on SiO ₂ %.....	72
Fig. 4.5 Effect of acid leaching temperature on SiO ₂ %.....	73
Fig. 4.6 Presence of oxide content in treated and untreated rice husk ash.....	73
Fig. 4.7 Effect of pH on different Na-silicate contents from 0.5 wt% to 3 wt% by diluting.....	79
Fig. 4.8 Corresponding pH as a function of H ₂ SO ₄ concentration	80
Fig. 4.9 Effect of Silica concentration on gelation time	81
Fig. 4.10 Effect of pH on gelation time	82
Fig. 4.11 Effect of Temperature on gelation time.....	83
Fig. 4.12 Precipitation process of silica	84
Fig. 4.13 Effect of Concentration of silica (%) on Syneresis (ml).....	84
Fig. 4.14 Effect of pH on syneresis (ml) at 1.5 % SiO ₂ and temp 25°C	85
Fig. 4.15 Effect of Temperature (°C) on syneresis at 1.5 % SiO ₂ and at pH 6	86
Fig. 4.16 As produced precipitated silica from rice husk ash.....	86
Fig. 4.17 XRD patterns of the as produced precipitated silica from rice husk ash.....	87
Fig. 4.18 FE-SEM images of precipitated silica at different magnifications (a) FESEM images of precipitated silica (1 μm ; X 10000); (b) FESEM images of precipitated silica (100 nm; X 30000).....	88

LIST OF TABLES

Table 2.1 Properties of sodium and silicon.....	8
Table 2.2: Physical properties of silicon dioxide.....	11
Table 2.3: Summary of the chemical reaction of silica with other chemicals	13
Table 2.4: Solubility of silicon dioxide in water at room temperature	14
Table 2.5: Different approaches to produce high purity amorphous silica from rice husk ash.....	22
Table 3.1: Rice husk ash collected from various rice mills in Bangladesh	36
Table 3.2: Summary of chemical used in this process.....	37
Table 3.3: Summary of reagents used in this research.....	38
Table 3.4: Summary of characterization equipment	39
Table 3.5: Diffraction peaks of crystalline silica	61
Table 4.1: Chemical composition analysis of rice husk ash by XRF	66
Table 4.2: Chemical analysis of rice husk ash	68
Table 4.3: The results of the acid leaching of rice husk ash	71
Table 4.4: Various analysis parameters used to produce sodium silicate from rice husk ash	75
Table 4.5: Results for the various analysis of produce precipitated silica from sodium silicate	77
Table 4.6: Characterization of products obtained from different stages of experiments	78
Table 4.7: Particle size analysis of as- produced precipitated silica from rice husk ash	88
Table 4.8: XRF analysis of as-produced precipitated silica from rice husk ash.....	89
Table 5.1: Cost analysis of different methods of producing precipitated silica.....	92

LIST OF ABBREVIATIONS

RHA	Rice husk ash
XRF	X-ray Fluorescence
XRD	X-ray Diffraction
SEM	Scanning Electron Microscope
FESEM	Field Emission Scanning Electron Microscope
FBC	Fluidized Bed Combustion
CAGR	Compound Annual Growth Rate
TSP	Triple Super Phosphate

CHAPTER ONE
INTRODUCTION

1. INTRODUCTION

1.1 Background of the Research

World's top tire manufacturers are preferring environmentally friendly production by incorporating a waste product created by the burning of rice husks into a valuable material named rice husk ash with considerable level of high-quality amorphous silica used in high-end tires. When precipitated silica from rice husk ash is added to a tire tread recipe, it helps reduce tires' road resistance, a phenomenon that causes vehicle engines to work harder and consume more fuel. "Low-rolling resistance" tires made with rice husk ash based precipitated silica also grip wet road surfaces better. These efforts are going to reduce the huge amount of rice husk ash entering the waste stream. Tire manufacturers are planning with the companies in Asia to eventually process ten thousand tons of silica from rice husk ash as over 90% of the world's rice is produced and consumed in the Asia-pacific region [1].

Most precipitated silica for tires and rubbers is produced using high temperature furnace method by incinerating sand at around 1382°C. But rice husk ash can be converted into usable silica for tires and rubbers at < 200°C because of the amorphous nature of silica, which is surely an economic advantage.

Global tire manufacturers hoped there would be momentum throughout the tire industry to use silica from rice husk ash. There is a concentrated effort underway in the tire industry to reduce its considerable carbon footprint. The ultimate goal of tire and rubber industry is to manufacture products using only renewable resources. Tire treads are composed primarily of natural and synthetic rubber, carbon black and oil. Those last three ingredients are petroleum-based, which has led manufacturers to explore the use of greener substitutes. Precipitated silica can reduce the amount of carbon black, but increases production costs of tire and rubber. Because tire grade precipitated silica with high surface area made from quartz sand by energy intensive furnace method, is very expensive (1200-1500 USD/MT) [2,3].

Besides this, precipitated silica has also been widely used in many applications including production of nanomaterials, plastics, in thickening and thixotropy of coatings and paints, printed inks, plastics and cosmetics, toothpaste, as desiccants, stabilizer, adsorbent, food rheology modifier and as carrier of pesticides and catalysts.

Technologies related to production method and applications of pure precipitated silica have been studied and developed throughout the world in great variety of ways. The production of silica at industrial scale is based on mechanical, physical, chemical, and energy-intensive thermal operations at high temperatures using large amounts of acids, generating significant volumes of effluents. The conventional silica production method is based on the reaction between sodium carbonate and quartz at high temperatures. After sodium silicate is formed, silica is precipitated in a reaction with sulfuric acid. But this method also consumes high levels of energy and produces large amounts of liquid effluents and greenhouse gases [4].

Recently, a large amount of precipitated silica has been extracted from various types of bio waste such as rice husk ash, bagasse ash, sugarcane ash, perlite, etc. Several techniques such as acid leaching or by gasification of rice hull with a pilot flame in a modified fluidized bed as well as by burning the rice husk ash at high temperature have been reported for the extraction of silica.

Rice husk has exclusive nanoporous silica layers, which have developed throughout years of natural evolution of the plant. This is why producing highly reactive silica from rice husk is a simple process with several advantages, compared with conventional production methods [5].

High purity is required in several applications of silica. Silica is a basic raw material widely used in the semiconductors, ceramics, polymers, and materials industries. This silica is usually produced from quartz fused at high temperatures, which affords to obtain ultrapure polycrystalline silicon and silicon hydride. In addition to environmental and economic advantages, low-energy, simpler methods to obtain pure silica create opportunities for the development of new industrial applications of rice husk ash.

1.2 Problem Statement

Production of precipitated silica in Bangladesh depends on the availability of two main raw materials including high quality quartz sand and soda ash, and fuel for high temperature furnace. Soda ash is usually imported; therefore, the inadequacy of the material poses a huge problem to the silica manufacturing industry. The shortage of natural gas for industrial sector in Bangladesh also creates an issue for manufacture. Burning coal in furnace causes an environment problem by emitting CO₂ in nature. Because of these negative issues, there is no single manufacturing plant of precipitated silica in Bangladesh. In contrast, rice husk ash being produced in abundance; though, an unutilized biomass posing environmental pollution and the difficulty in their use will be a good source of silica for precipitated silica manufacturer. The hydrothermal route of producing silica from rice husk ash requires lesser temperature consumption hence, will be a better method of producing precipitated silica. This process would reduce the cost of production in addition to preventing the environmental pollution associated with the ash disposal.

1.3 Objectives of the Research

The objective of this research is to design and develop an economical manufacturing route for the production of precipitated silica from rice husk ash by alkaline extraction of amorphous silica, followed by precipitation of alkaline silicate at lower temperature compared to conventional method. The research includes investigation of the optimum reaction parameters of extraction and precipitation of silica from rice husk ash and to improve the quality and quantity of silica production.

An alternative approach to synthesis of low-cost precipitated silica from plant bio-waste such as rice husk ash which has a significant source of high purity silica has only been explored by relatively few research groups. However, the narrow and isolated experimental conditions of previous works and lack of an optimized process have limited the engineering application of such results. The lack of a commercially viable route for synthesis of bulk high purity silica provides a good motivation to conduct further research into the feasibility of this approach. The present study has been undertaken to evaluate systematically and quantitatively the influence of various physical and chemical factors on the extraction of pure precipitated amorphous silica from rice husk ash, an abundant solid waste. Rice husk ash containing high silica content can be an economically viable raw material for production of pure precipitated silica.

The objective of this research is to investigate the possibility of producing low cost precipitated silica from rice husk ash by:

- To obtain amorphous silica rich rice husk ash by removing metal impurities using acid leaching method.
- To synthesize precipitated silica from locally available rice husk ash (as-received) at comparatively lower temperature by hydrothermal treatment to produce alkaline silicate followed by acid assisted precipitation of produced silicate.
- To identify and optimize reaction conditions for each step of the process.
- To study the fundamentals involved in the major purification process.
- To investigate physical and chemical properties of precipitated silica with increasing and decreasing of different reaction variables.
- To investigate the physicochemical properties of rice husk ash and precipitated silica by XRF, use of XRD to identify the pattern of silica in rice husk ash and precipitated silica and FESEM used to observe the topography and morphology.
- To optimize a feasible and cost-effective manufacturing technology of precipitated silica in perspective of Bangladesh.

These findings will assist in developing a feasible route for the production of high purity precipitated silica from locally available rice husk ash. This research will also facilitate in waste management since no other suitable way is found to dispose of these rice husk ashes. This newly developed method to produce precipitated silica will help to fulfill the local demand in our industrial sector. These endeavors, all together, will help to maintain not only disposal of rice husk ash but also save our local currency.

1.4 Outline of the Thesis

This thesis consists of six chapters. Chapter one introduces the research topic covered by this thesis. It includes background of research, problem statement, objectives, and research outline.

Chapter two reviews the up to date research progress on precipitated silica manufacture from rice husk ash. This chapter also describes the specifications of rice husk ash and economical point of view with new features of the research.

Chapter three represents the development of cost-effective method of manufacturing precipitated silica. The method will be used as a performance evaluation tool to study the effect of various physical and operating conditions. This chapter also describe characterization techniques of rice husk ash, alkaline silicate and precipitated silica. The characterization techniques consist of physicochemical analysis of rice husk ash, sodium silicate and precipitated silica. SEM analysis to determine morphological characteristics and XRD analysis for phase identification. Different experimental methods to determine various properties of rice husk ash, silicate and silica are also discussed in this chapter.

Results and discussions have been described in chapter four. Which include the effect of operating conditions on rice husk ash, process and procedures to prepare silica theoretically and experimentally. These operating conditions are temperature, reaction period, water content and strengths of chemicals used in reactions. This chapter also represents elemental and quantitative analysis, phase and morphological analysis of rice husk ash, sodium silicate and precipitated silica.

Chapter five will provide cost analysis and comparisons with conventional and existing manufacturing methods of precipitated silica and will explain how this process will more cost effective than existing's.

The major findings from the study are summarized and possible future research topics are suggested in chapter six.

CHAPTER TWO
LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 Silicon Dioxide

Silicon dioxide, also known as silica (from the Latin *silex*), the name given to a group of minerals composed of silicon and oxygen, the two most abundant elements in the earth's crust, is an oxide of silicon with the chemical formula SiO_2 , most commonly found in nature as quartz and in various living organisms. In many parts of the world, silica is the major constituent of sand. Silica is one of the most complex and most abundant families of materials, existing as a compound of several minerals and as synthetic product. Notable examples include precipitated silica, fumed silica, silica gel, and colloidal silica [6].

Silicon dioxide is found in nature in mainly two forms: crystalline and amorphous. Silica is also a constituent of gemstones, and traces of the compound have also been found in volcanic rocks. It is the most abundant compound of silicon found on the earth's crust, and one of the most commonly found oxides. Silica in rice husk ash remain in amorphous form, while quartz is an example of crystalline silica. Table 2.1 and Fig. 2.2 shows the properties of sodium and silicon and optical images of crystalline and amorphous silica respectively.

Table 2.1 Properties of sodium and silicon

<u>Sodium</u>	<u>Silicon</u>
<ul style="list-style-type: none">▪ Group number: 1 A (alkali metals)▪ Period: 3▪ Electron configuration: $1s^2 2s^2 2p^6 3s^1$▪ Positive ionic charge▪ Lose 1 electron to form an ion	<ul style="list-style-type: none">▪ Group number: 14▪ Period: 3▪ Electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^2$▪ Common ionic charges: none▪ State of matter at 25°C: solid

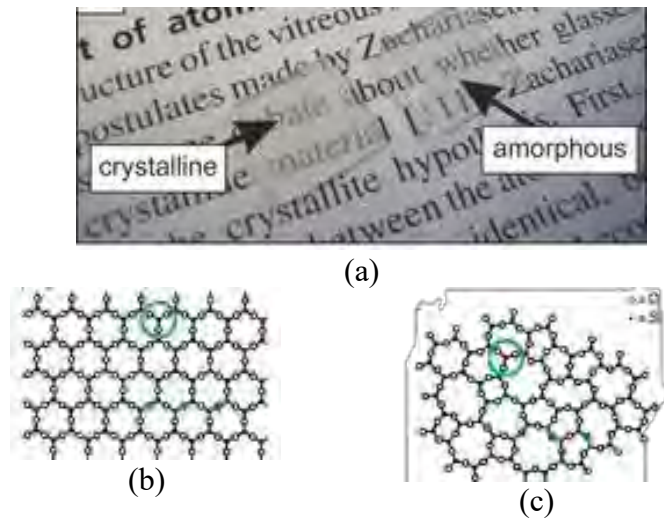


Fig. 2.1 (a) Optical image of crystalline and amorphous silica; (b) Structure of crystalline silica; (c) Structure of amorphous silica [8].

2.1.1 Molecular structure of silicon dioxide

Silica occurs in nature in more than 13 different structures, each one slightly varying from the others. The physical properties might be different but the chemical properties remain the same, irrespective of the structure. In order to get a better understanding of its many properties, it is important that we have a basic idea about the molecular structure of this oxide of silicon [9, 10]. The building block of the structure of silica is the SiO_4 unit. The structure of crystalline forms of silica is represented as continuous links of the SiO_4 unit. The silicon dioxide molecule can be described as a three-dimensional network of tetrahedra cells, with four oxygen atoms surrounding each silicon ion, shown in Fig. 2.2 (a). The length of a Si-O bond is 0.162 nm, while the normal distance between two oxide bonds is 0.262 nm. The Si-Si bond distance depends on the SiO_2 arrangement, but is approximately 0.31 nm and the bond angle O-Si-O is approximately 109° . The bond angle Si-O-Si is ideally approximately 145° , but it can vary between 100° and 170° with minimal change in bond energy. The tetrahedral form is the basic unit from which a SiO_2 structure is formed, even though SiO_2 can exist in a crystalline structure. The reason for the amorphous oxide structure is the absence of any crystalline form of SiO_2 whose lattice size closely matches the silicon lattice. The tetrahedra bond together by sharing oxygen atoms as illustrated in Fig. 2.2 (b) in a sample six-membered ring [11].

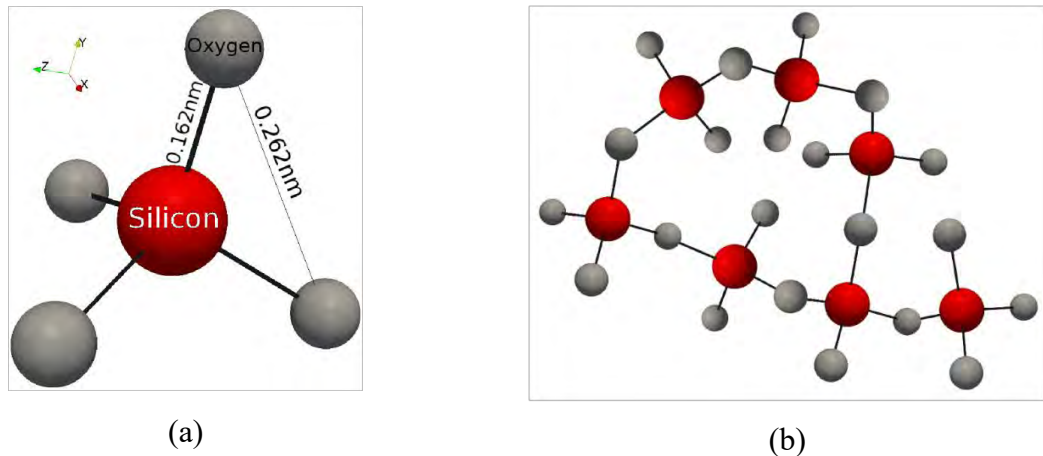


Fig. 2.2 (a) Structure of fused silica glass along with; (b) a six-membered ring structure of SiO_2 [11].

Here are some facts about the molecular structure of silicon dioxide.

- The angle formed between each $-\text{O}-\text{Si}-\text{O}-$ bond is 109.5 degrees. However, in quartz, this angle is around 144 degrees.
- There is uneven charge distribution between parts of the tetrahedron, with the center being highly positive and the corners being strongly negative. This is because of the strong polarity of the Si-O bond.
- In gaseous state, the structure of silicon dioxide forms linear $\text{O}=\text{Si}=\text{O}$ molecules.
- Each individual SiO_4 tetrahedron is connected with adjacent tetrahedrons at the corners, forming a three-dimensional structure.
- The "bridge" formed by the oxygen atoms, between the silicon atoms of adjacent tetrahedrons, is responsible for some of the unique properties of silicon dioxide.
- The tetrahedral shape is responsible for the rigidity of the silicon dioxide molecule.
- The length of the Si-O bond is 0.162 nm and O-O bond is 0.262 nm [9].

It might be wondering why the molecular formula of silicon dioxide is SiO_2 when the structure shows four atoms of oxygen surrounding each silicon atom. The reason is every individual tetrahedron shares each of its four oxygen atoms with the neighboring tetrahedron, which makes the net chemical formula to be SiO_2 .

2.1.2 Physical properties of silicon dioxide

Due to the tetrahedral structure, the melting point of silicon dioxide is very high. The strong silicon-oxygen covalent bonds get broken at very high temperatures, close to 1700°C. Also, silicon dioxide is very hard and rigid, and this is again due to the strong covalent bond between silicon and oxygen. Due to the absence of free electrons within the molecular structure, silicon dioxide is a very poor conductor of electricity, and acts as an insulator. Silicon dioxide is insoluble in water and in all organic solvents. However, it is soluble in alkalis and hydrofluoric acid. The table given below enlists the values for some of the physical properties of silicon dioxide, both crystalline and amorphous [9].

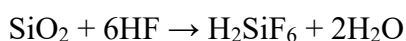
Table 2.2: Physical properties of silicon dioxide [9]

Physical Property	Unit	Crystalline Silica (Quartz)	Amorphous Silica
Melting Point	°C	approx. 1700	approx. 1700
Density	g cm ⁻³	2.6	2.2
Refractive Index	-	1.46	1.46
Resistivity	ohm-cm	10 ¹² - 10 ¹⁶	greater than 10 ¹⁸
Thermal Conductivity	Wm ⁻¹ K	1.3	1.4
Poisson's Ratio	-	0.17	0.165
Coefficient of Thermal Expansion	K ⁻¹	7.64 x 10 ⁻⁷	5.4 x 10 ⁻⁷

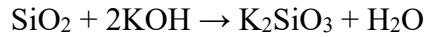
2.1.3 Chemical properties of silicon dioxide

At room temperature, SiO₂ in all modifications is almost inert and does not react with most other substances. Even at moderately high temperatures silica is chemically very stable. For that reason, fused quartz (silica glass) is widely used for chemical apparatus, especially when catalytic reactions of the metal cations in ordinary glass need to be avoided. The reason for the low reactivity of silica is the very strong Si-O bond, but also its macromolecular structure [12]. A few salient chemical properties of silica are:

- Being the anhydrite of an acid itself (orthosilicic acid, H₄SiO₄), quartz in general will not be attacked by acids. The prominent exception is hydrofluoric acid (HF) [13], which will decompose quartz to form first silicon fluoride SiF₄, then hydrofluorosilicic acid:

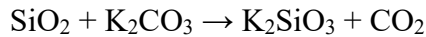


- SiO₂ is also attacked by alkaline substances (like potassium hydroxide, KOH). The speed of the reaction depends on the modification and crystal size. Crystalline quartz will dissolve very slowly in hot watery alkaline solutions, while amorphous SiO₂ will be readily dissolved at room temperature:

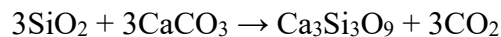


- A similar reaction leads to the formation of silica gels in concrete, when the alkaline compounds of the concrete, typically Ca(OH)₂ react with amorphous silica and cryptocrystalline quartz (that is, opal and chalcedony). The silica gel attracts water, swells and cracks the concrete within a few decades.

- All forms of silica dissolve in molten natron (Na₂CO₃) or potash (K₂CO₃) to form silicates:

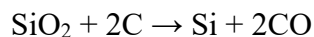


- At high temperature, many geological environment's quartz acts as an acid and reacts with many alkaline minerals. A well-known example is the formation of the mineral walstromite Ca₃Si₃O₉ from quartz and calcite in contact metamorphic processes at temperatures from about 600°C upwards:



- The opposite reaction takes place at the weathering of silicate rocks, here the carbonic acid (H₂CO₃) present, for example, in meteoric waters releases silicic acid and forms carbonate [14].

- Quartz is the "ore" of silicon. Silicon is retrieved at a temperature of about 2000°C in the following endothermic (energy-consuming) reaction:



- The Si-O bond is much stronger than the C-O bond, and the reaction only works because carbon monoxide (CO) escapes from the system as a gas, so the system's equilibrium is pushed to the right side. The formation of carbon monoxide instead of carbon dioxide CO₂ is typical for reductive reactions with carbon at high temperatures. The silicon formed in this process is not pure enough for chip production and needs to be purified in a rather complex procedure. So, despite the abundance of its ore, pure silicon is relatively expensive.

A summary of the different chemical reactions of silica with other chemicals has been given in Table 2.3.

Table 2.3: Summary of the chemical reaction of silica with other chemicals

Reacting Substance	Reaction Conditions	Main Product Formed	Chemical Equation
Strong alkalis such as sodium hydroxide (NaOH) and potassium hydroxide (KOH)	Crystalline silicon dioxide dissolves very slowly in hot alkaline solutions, whereas its amorphous form reacts with alkalis at room temperature.	Silicates of potassium or sodium	$\text{SiO}_2 + 2\text{KOH} \rightarrow \text{K}_2\text{SiO}_3 + \text{H}_2\text{O}$ $\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$
Hydrofluoric acid (HF)	Quartz does not react with other acids but dissolves in hydrofluoric acid, and the reaction takes place at room temperature.	Hydrofluorosilicic acid (H_2SiF_6)	$\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$
Sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3)	Silicon dioxide reacts with molten carbonates of sodium and potassium.	Silicates of sodium and potassium (K_2SiO_3 and Na_2SiO_3)	$\text{SiO}_2 + \text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{SiO}_3 + \text{CO}_2$ $\text{SiO}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2$
Calcium carbonate (CaCO_3)	At very high temperatures above 600°C , quartz reacts with alkaline substances such as limestone or calcium carbonate.	Calcium silicate ($\text{Ca}_3\text{Si}_3\text{O}_9$), commonly known as walstromite	$3\text{SiO}_2 + 3\text{CaCO}_3 \rightarrow \text{Ca}_3\text{Si}_3\text{O}_9 + 3\text{CO}_2$
Carbon	Natural silica or quartz reacts with carbon at around 2000°C to give silicon. This reaction is used for obtaining silicon from its ore.	Silicon (Si)	$\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$
Water	Under high temperature and pressure conditions, silica is hydrolyzed by water to form hydroxide of silicon, which is highly unstable.	Silicon hydroxide ($\text{Si}(\text{OH})_4$)	$\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Si}(\text{OH})_4$

2.1.4 Solubility of silica in water

The solubility of silicon dioxide in water is dependent on temperature, pressure and, surface structure [15]. The following table gives an overview of the solubility at room temperature and normal pressure.

Table 2.4: Solubility of silicon dioxide in water at room temperature [15]

Different structures of silicon dioxide	Solubility in Water at 25°C
Microcrystalline quartz	2.9 mg/l / 6-11 mg/l
Chalcedony	22-34mg/l
Cristobalite	6 mg/l
Tridymite	4.5 mg/l
Stishovite	11 mg/l
Quartz glass (amorphous)	39 mg/l / 120 mg/l

2.1.5 Uses of silicon dioxide

One of the most common uses of silicon dioxide is in food rheology modifier, where it is used as an additive, emulsifiers and anti-caking agent. Following are some other important applications of silicon dioxide.

- Amorphous silica is added as fillers to the rubber during the manufacturing of tires.
- Quartz is used in the glass industry as a raw material for manufacturing glass.
- Silica is used as a raw material for manufacturing concrete as a reactive pozzolan.
- Silica is added to varnishes because of its hardness and resistance to scratch.
- Silica is used in the production of silicon.
- Due to the fact that silica is a good insulator, it is used as a filler material in electronic circuits.
- Because of its piezoelectric properties, quartz is used in transducers.
- It is a substance used for making optical fibers.
- Due to its ability to absorb moisture, silica is used as a desiccant.

2.2 Silicon Dioxide – Amorphous Form

The desirable physicochemical and mechanical properties of amorphous silica, notably their mechanical resistance, high dielectric strength, and selectivity for chemical modification, amorphous silica has become a key material in semiconductor, microelectronics and chromatography [16]. Because of its unique properties, silica is quintessential for a broad range of applications such as chips, optical fibers, and telescope glasses. Furthermore, molecular biologists employ silica in resins and optical beads to study the biomacromolecules [16]. Although hosts of synthetic amorphous silica are produced commercially, the ones produced from plant origins such as rice husks have been noted to have some significant advantages over those from mineral and synthetic origins [17]. The Dictionary of Composite Materials Technology [18] defines amorphous silica as a naturally occurring or synthetically produced oxide of silicon characterized by the absence of a pronounced crystalline structure and whose X-ray diffraction patterns have no sharp peaks. This type of silica may be anhydrous or have a significant water of hydration in its structure. In particular, the processing steps for extracting amorphous silica from plant source are relatively simple and require no elaborate infrastructure or consumption of costly reagents as in the case of the synthetic processes. In addition, the final silica powder produced from plant sources contains a narrow range of metal oxide impurities, which makes them exceptionally desirable in applications where high purity silica at modest cost is a necessary prerequisite [17]. A typical X-ray diffraction pattern of amorphous silica produced from rice husk combustion is shown in Fig. 2.3 [19].

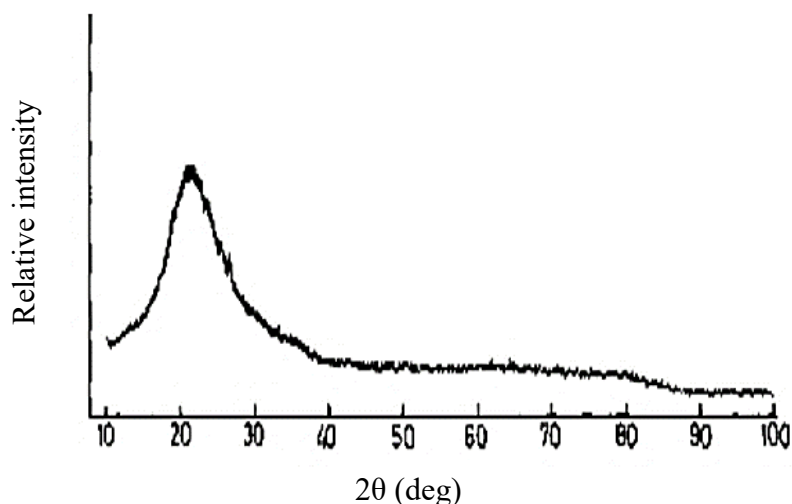


Fig.2.3 Typical XRD pattern of amorphous silica from RHA [19].

The classification of amorphous silica into gel or powders largely depends on the bond strengths between the ultimate colloidal particles. Silica gels are characterized by a coherent three-dimensional network of contiguous particles whilst silica powders consist of small granules of silica gel or aggregates of submicron particles that are weakly linked together [19].

Precipitated silica is an amorphous form of silicon dioxide (SiO_2) produced by precipitation from a solution containing silicate salts. It is a relatively pure form of the mineral silica, which is produced by the chemical process known as precipitation. Sodium silicate and sulfuric acid are the raw materials used to produce precipitated silica. Large quantities of these materials are mixed with water simultaneously in measured amounts while under constant agitation. The two chemicals react with each other as sodium silicate is alkaline and sulfuric acid is a strong oxidizer. The overall pH of the mixture is kept alkaline, because the precipitation reaction is not as vigorous under neutral or acidic conditions. While other acids would also work to create the conditions necessary to precipitate silica. However, sulfuric acid is used almost exclusively [20].



Fig. 2.4 Structure of precipitated silica [20].

In chemical precipitation, a solid form from a liquid due to a chemical reaction. Precipitated silica is formed by mixing solutions of sodium silicate with sulfuric acid in water. A chemical reaction occurs, and pellets of pure silica form. The physical properties of the resulting silica can vary slightly depending on the exact conditions under which the precipitation reaction takes place. Changes in temperature, concentration of the solutions used, and the ratio of the ingredients in the mixture can all alter the physical properties of the silica particles. Manipulating these conditions lead to change the size and porosity of the silica grains [20].

After the silica has formed, it is separated from the solution, cleaned, and dried. This involves washing the silica to remove all traces of chemical salts and by-products of the precipitation process. The washing and drying process can also affect the character of the particles [20]. Particle size, porosity, and density can all be manipulated this way to some extent. Manufacturers can prepare precipitated silica in a number of ways depending on its intended use by the customer.

2.2.1 Physicochemical properties of precipitated silica

BET surface area

Brunauer, Emmett and Teller developed the process of calculating the surface area of precipitated silica. This method of calculating the surface area is popularly known as BET surface area.

pH value

The pH value of precipitated silica is generally in neutral range. It is determined electrometrically with a glass electrode and pH meter.

Drying loss

There is very small amount of physically bonded water content in precipitated silica. The major part of this water content is removed by drying in drying cabinet at 105°C for 2 hours.

Ignition loss

Precipitated silica contains chemically bonded water in the form silanol groups is also removed after 2 hours of ignition time at 1000°C. The ignition loss is determined with the substance that has previously been dried for 2 hours at 105°C [21].

SiO₂ content

Silicon dioxide content is determined either gravimetrically by fuming off with hydrofluoric acid, or by X-ray fluorescence (XRF).

Sieve residue

Sieve residue is determined by using Mocker apparatus. In this process the silica suspension is washed through the sieve with 4 bar water pressure. 45-micron sieves (325 mesh) is used for this process. The sieve is then dried and sieves residue is weighed.

Tamped density

The tamped density is calculated from the initial weight of the sample and the resulting volume, reported in g/l. It is used for the purpose of calculating weight of product in powder form.

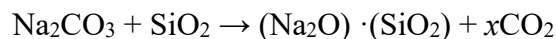
DBP absorption

The DBP absorption is a numerical value used to indicate absorptive capacity of filler. Owing to the automatic measurement process, this method can be carried out more accurately than the determination of the oil absorption. The DBP absorption capacity is influenced by other parameters, such as the particle size.

2.2.2 Manufacturing process of precipitated silica from silica source

Manufacturing process of Precipitated silica is commonly divided into two stages including silica extraction by alkaline solution and silica precipitation by acid.

Extraction of silica from silica sand as sodium silicate is commonly done by roasting soda ash (sodium carbonate, Na₂CO₃) and silica sand (a ubiquitous source of SiO₂) in a furnace at temperatures between about 1000-1400°C, a process that gives off carbon dioxide (CO₂) and produces sodium silicate (Na₂SiO₃); usually represented by its two constituents, Na₂O and SiO₂ [22]:



This roasting produce fused glassy lumps called cullet, which can be fed into pressurized reactors for dissolving in hot water. The solution is cooled to a viscous liquid and used to produce precipitated silica [23].

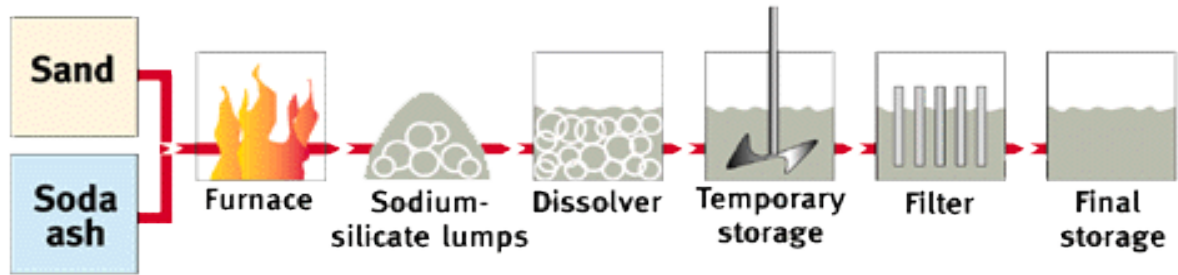


Fig. 2.5 Basic flow diagram of producing sodium silicate by furnace route.

Sodium silicate liquid can also be prepared directly by dissolving silica sand at high pressure in a heated aqueous solution of caustic soda (sodium hydroxide, NaOH):

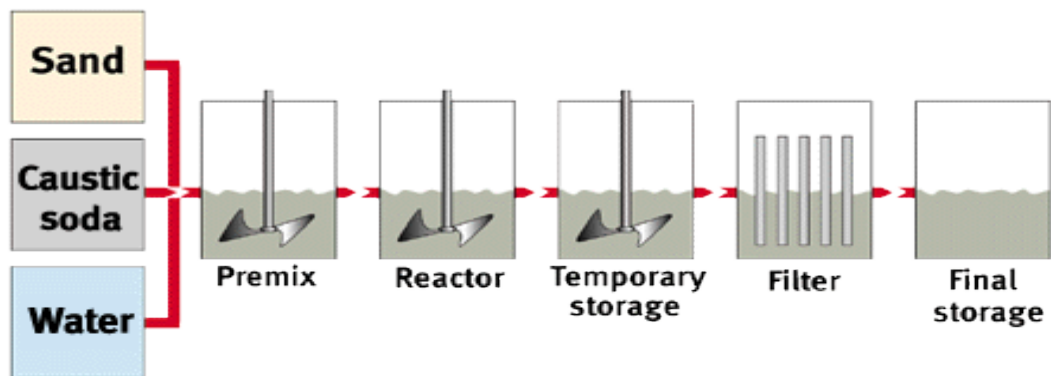
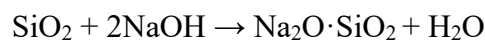
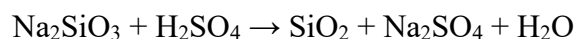


Fig. 2.6 Basic flow diagram of producing sodium silicate by hydrothermal route.

The production of precipitated silica starts with the reaction of an alkaline silicate solution with a mineral acid (mostly sulfuric acid). Sulfuric acid and sodium silicate solutions are added simultaneously with agitation to water. Precipitation is carried out under alkaline conditions. The choice of agitation, duration of precipitation, the addition rate of reactants, their temperature and concentration, and pH can vary the properties of the silica. The formation of a gel stage is avoided by stirring at elevated temperatures. The resulting white precipitate is filtered, washed and dried in the manufacturing process.



Amorphous silicate powders are prepared by drying aqueous solutions by means of spray or drum dryers. These products may then be further treated in order to modify powder properties, e.g. particle size, bulk density [24].

Rice husk ash, a waste product generating from rice mills is rich in silica. Several methods have been developed by research groups to produce pure amorphous silica from rice husk ash. Among them few methods developed based on alkaline extraction followed by acid precipitation. A simple method based on alkaline extraction followed by acid precipitation was developed by U. Kalapathy [30] to produce pure silica xerogels from rice husk ash, with minimum mineral contaminates. Xerogels produced from rice husk ash had 93% silica and 2.6% moisture.

An inexpensive chemical method was used by Sanker et al. [25] to synthesize biogenic mesoporous silica from rice husk ash. The microstructure, elemental, chemical bonding, functionality, porosity, and mass-loss of mesoporous silica nanopowder were evaluated by different characterization techniques.

High purity silica was produced by Bakar et al. [26] through controlled combustion of rice husk after acid treatment. In this study, leaching of rice husk with hydrochloric acid and sulfuric acid were carried out prior to combustion to obtain pure silica. Liou and Yang [27] investigated a dissolution-precipitation technique as a function of acid treatment, sodium silicate concentration, gelation, pH, aging temperature and aging time to establish optimum conditions for preparing silica nanoparticles.

A recyclable technology was developed for preparation of silica powder using rice husk ash and NH_4F by Xiaoyu Ma et al. [14]. The microstructure and morphology analysis of the precipitated silica powders were characterized in this study. A new process for the synthesis of zeolites and wollastonite from RHA colloidal silica was developed by Fernandes [28]. The process was aimed at lower energy costs, fewer stages and fewer reactants consume.

The potential and limits of rice husk to prepare relatively pure activated silica were investigated through the study of Yalcin [29]. For the activated silica, rice husk samples were submitted to a chemical pre-and post-treatment using HCl , H_2SO_4 and NaOH solution. After incinerated at 600°C under static air and flowing atmospheres, the final product was characterized in terms of silica content, particle size distribution and morphology, specific surface and porosity. On the other hand Conradt et al. [31] in their study used chemical pre-treatment using cellulose enzyme, NaOH , HCl , H_2SO_4 solution.

Silica originating from rice husks has been proposed by Riveros and Garza [32] for use in the manufacture of solar cells. In this study 99.98% pure silica was obtained for further investigation of manufacturing of solar cells.

Table 2.5: Different approaches to produce high purity amorphous silica from rice husk ash

Study	Objective	Summary of method used	Main results
Sankar et al. [25]	To produce nanosilicon powder from three kinds of rice husk.	<ul style="list-style-type: none"> ▪ Combustion of rice husk in the open furnace. ▪ Acid leaching ▪ Incineration at 700°C under atmospheric conditions 	Spherical, completely amorphous silica particles with large specific surface area and composed only by Si and O from all kinds of rice husk.
Bakar et al. [26]	To investigate the ideal conditions to obtain high purity silica.	<ul style="list-style-type: none"> ▪ Washing of rice husk with water ▪ Acid leaching ▪ Incineration at 500, 600, 700, 800, and 900°C for 2 h under atmospheric conditions 	All silicas had amorphous particles, and rice husk leached with HCl produced the highest content of silica (99.582%) at 600 °C.
Ma et al. [14]	To develop a new, recycling-based technique to produce silica from rice husk ash.	<ul style="list-style-type: none"> ▪ Acid leaching of rice husk ash ▪ Extraction in reactor with NH₄F ▪ Acid precipitation of silica 	Spherical, completely amorphous silica particles measuring 50 to 60 nm in diameter and containing only Si and O, with yield of 94.6%.
Liou and Yang [27]	To investigate the effect of experimental conditions on the characteristics of the nanosilica obtained.	<ul style="list-style-type: none"> ▪ Leaching of rice husk with water and then HCl ▪ Incineration ▪ Extraction with NaOH, forming silicate ▪ Precipitation 	Best results with pH 3, silicate 0.15 M, aging time of 12 h at 50 °C, with 99.48% purity silica.
Fernandes [28]	To evaluate the leaching of rice husk ash with NaOH to easily obtain highly reactive colloidal silica.	<ul style="list-style-type: none"> ▪ Extraction of silica with NaOH 1M ▪ Precipitation using H₂SO₄ drop by drop 	The best Si:Na mass ratio was 4:1, and the highly reactive colloidal silica was obtained at low energy investment.
Yalçın and Sevinç [33]	To obtain high purity silica with large specific surface area and to evaluate the competitiveness of silica from rice husk.	<ul style="list-style-type: none"> ▪ Washing of rice husk with water ▪ Chemical treatments (acid leaching, alkaline leaching) ▪ Incineration at 600°C under different conditions (static oven, argon flow, oxygen flow, air flow) 	Amorphous silica particles with maximum specific surface area of 321 m ² /g 99.66% purity, depending on the treatment. The highest purity silica was obtained with prior acid treatment and incineration in oxygen atmosphere.
Kalapathy et al. [30]	Investigate the efficacy of acid leaching of rice husk ash before alkaline extraction and washing of silica obtained with water.	<ul style="list-style-type: none"> ▪ Acid leaching ▪ Extraction of silica with NaOH ▪ Precipitation with HCl ▪ Washing with water 	Initial acid leaching did not improve purity, the washing with water reduced Na and K levels, and silica yield was excellent when extraction was carried out with NaOH 1 N.
Conradt et al. [31]	To obtain high purity silica with large specific surface area and to evaluate the competitiveness of silica from rice husk.	<ul style="list-style-type: none"> ▪ Washing rice husk with water ▪ Different chemical treatments (acid leaching, alkaline leaching, and enzymatic digestion) ▪ Incineration at 600°C ▪ (static oven, argon flow, oxygen flow, air flow) 	Except for leaching with NaOH, all other treatments produced amorphous silica with large specific surface area, and high purity silica was obtained with acid leaching with HCl.
Riveros and Garza [32]	To optimize the production of silica from rice husk.	<ul style="list-style-type: none"> ▪ Washing rice husk with water ▪ Acid leaching ▪ Incineration ▪ Leaching of rice husk ash 	Silica with approximate purity of 99.98% with three washing cycles, 6-h acid leaching, 6 leaching cycles with HCl 3% at 90°C, and the main contaminant was Ca (100 ppm).

Table 2.5 makes it clear that many approaches have been developed to produce high purity amorphous silica with large surface area using rice husk or rice husk ash. Several studies used alkaline extraction sol-gel method, which forms silicates, followed by silica precipitation by reaction with an acid.

From the state-of-the-art literatures it is established that amorphous silica from rice husk ash can be obtained by alkaline extraction at low temperature. Also, at pH below 10, the solubility of amorphous silica is very low, but it rises suddenly when pH is increased above that. This solubility profile affords to extract silica from rice husk ash by solubilization in alkaline medium and subsequent precipitation at lower pH values. Consuming comparatively lower amounts of energy, the alkaline extraction of silica by solubilization is not as costly or damaging to the environment as that of quartz fusing method.

Chemical and mechanistic aspects of silica formation

Amorphous silica is formed by a complex inorganic polymerization process with orthosilicic acid as the monomeric building block. Solubility of monosilicic acid $\text{Si}(\text{OH})_4$ is limited to a concentration of 2 mM in aqueous solutions of neutral pH and de-protonation at pH values above 9 gives silicate anions $\text{SiO}(\text{OH})_3^-$ [34,35]. Nucleophilic substitutions between silicate anions and silicic acid molecules lead to condensation reactions that form siloxane bonds (Si-O-Si). Silicic acid molecules react to form highly dense, branched polysilicic acid species. These colloidal silica particles have sizes in the nanometer range. Depending on the pH and the presence of salts or other additives such as silica sol can undergo a variety of reactions. At pH values below 7, there is only weak electrostatic repulsion between the colloidal silica particles due their uncharged surfaces and the colloidal particles aggregate to fibrillar, branched chain forming a gel. At pH values above 7, negative charges on the surfaces of the colloidal silica particles dominate and induce electrostatic repulsion. Therefore, colloidal silica particles form a stable sol and the particles grow by the Ostwald ripening process [34,36]. The addition of a cationic flocculant to a silica sol leads to fast precipitation of silica particles. Cationic species adsorb to silica surfaces and bring them close together resulting in coagulation of particles. Alternatively, cationic species, e.g., polyamines are suggested to stabilize the pentavalent transition state of the condensation reaction between silicic acid molecules and therefore further promote silica flocculation [31,37,38].

2.3 Demand of Precipitated Silica in Various Market

2.3.1 Precipitated silica market worth 2.23 billion USD by 2021

The global precipitated silica market is projected to reach USD 2.23 billion by 2021, at a CAGR of 9.1% from 2016 to 2021. High demand for precipitated silica from the tire and rubber products industry is expected to drive the growth of the market in near future [39].

Precipitated silica market, by geography, 2021 (USD Billion)

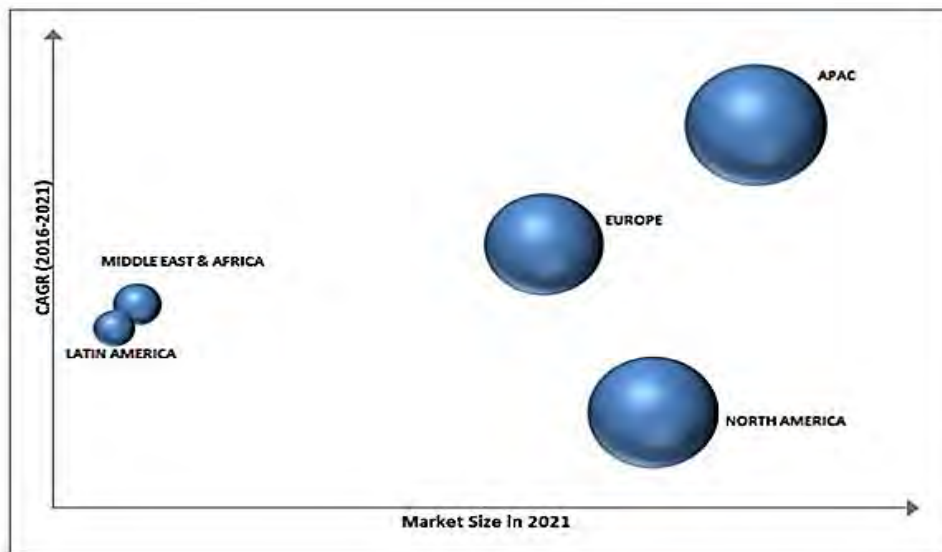


Fig. 2.7 Global precipitated silica market by geography [39].

Automobile end-use industry segment contributed the largest share to the precipitated silica market, by end-use industry in 2015, and is projected to be the fastest-growing end-use industry segment from 2016 to 2021. This growth can be mainly attributed to the increased demand of precipitated silica from the automotive tire industry, as precipitated silica provides enhanced properties to the tire such as reduced rolling resistance, increased traction, and high wear resistance [39].

Rubber segment contributed the largest share to the precipitated silica market, by application in 2015, and is projected to be the fastest-growing application segment from 2016 to 2021. This growth can be attributed to the increased demand of precipitated silica in rubber products, as it acts as a reinforcing filler and increases the strength and durability of rubber [40].

Asia-Pacific was the largest market for precipitated silica market in 2015, owing to the rise in demand of precipitated silica in this region. This increased demand can be attributed to the growing demand for automotive tires, personal care products such as toothpastes, footwear, and pesticides in the region. China, India, and Japan are the leading countries in terms of production and consumption of precipitated silica in Asia-Pacific. Low cost of raw materials and labor as well as the high demand from end-use industries such as tires, toothpastes, and others are expected to drive the growth of the precipitated silica market in these countries.

Key players operational in the precipitated silica market include Evonik Industries AG (Germany), PPG Industries Inc. (U.S.), W.R. Grace and Co. (U.S.), Tosoh Silica Corporation (Japan), Solvay SA (Belgium), Huber Engineered Materials (U.S.) and Oriental Silica Corporation (Taiwan) [41].

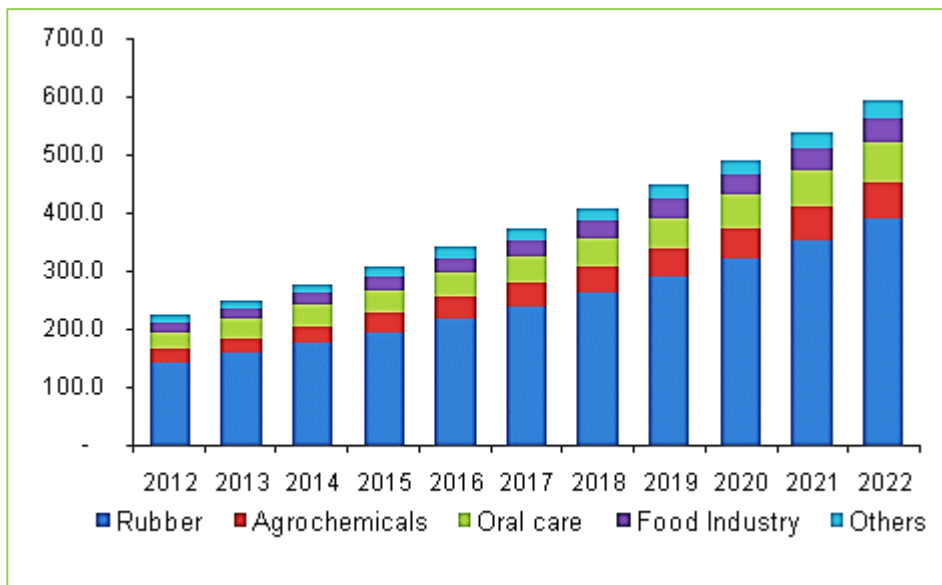


Fig. 2.8 U.S Precipitated Silica market revenue, by application, 2012 - 2022 (USD Million) [41].

2.3.2 Analysis of imports of precipitated silica from India to Bangladesh

India is the major exporter of precipitated silica to Bangladesh and exported worth USD 2.24 million with total quantity of 2,190 MT from 2014-2016. Mundra accounted for 79.4% of exports followed by Petrapole Road and Sabarmati ICD which account for 10.5% and 7.5% of exports respectively. Average price of precipitated silica per kg is USD 1.02 and average value per shipment is 11.8 MT.

Fig. 2.9 shows the quantity (line) and value (bar) of imported precipitated silica form India.

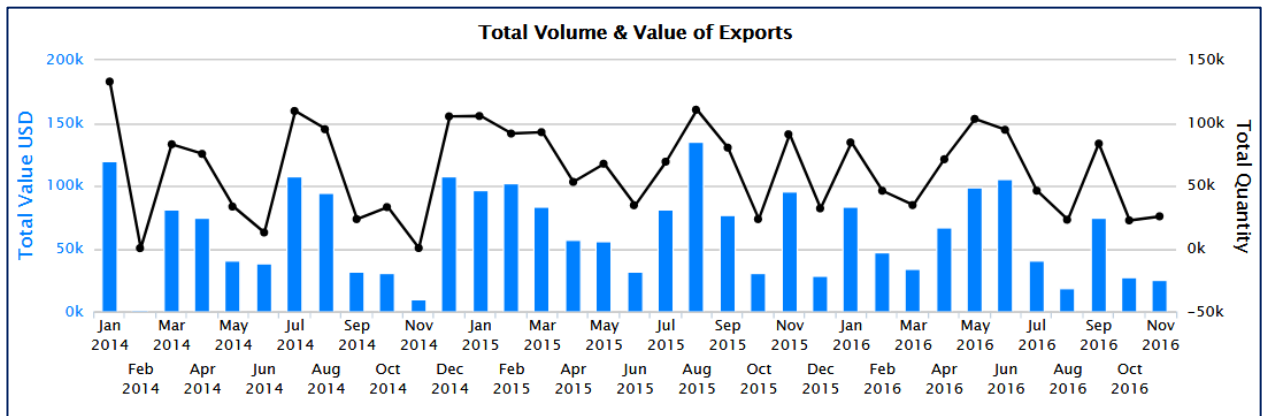


Fig.2.9 Total quantity and value of imports of precipitated silica 2014 – 2016 [42].

2.4 Industrial Application of Precipitated silica

2.4.1 Non-rubber grade precipitated silica

Toothpaste and toothpowder

Precipitated silica is used in manufacturing transparent and medicated toothpaste wherein it acts as cleaning, polishing, and whitening agent. The product is used as mild abrasive cleaners and thickeners owing to maximum fluoride compatibility. Furthermore, the compound is used in toothpaste formulations on account of its whitening and cleaning properties to meet dentifrice applications. These products act as thickeners to maximize the fluoride compatibility and help minimize tooth sensitivity.

Precipitated silica used in oral care was valued at over USD 180.0 million in 2014 [43]. The increasing use of the product in toothpaste industry is expected to propel the market demand over the forecast period. Growing use of dental silica as thickeners in toothpaste improves the shelf life of the product. Additionally, this product also acts as thickeners and cleaning agents in varied dentifrice products owing to its compatibility with organic hydrocolloids.

Pesticides

Precipitated silica is used as a carrier and diluent in pesticides. In comparison with cheaper clays, it has high absorption, easier suspensibility, better compatibility with most toxicants and better stability even after extended storage under tropical condition [44].

Printing ink

Precipitated silica is used as a thickening and suspending agent to prevent set off, picking, and heighten brilliance [44].

Salt

Precipitated silica provides free flowing characteristics in salt and prevents caking. It does not have any effect on taste, odor, color and nature of the salt [44].

Coatings

Precipitated silica is used as thickening, thixotropic, antissettling agent and as matting agent at high concentration. It also reduces gloss and gives satin sheen in nitrocellulose furniture lacquer. It is also preferred in aluminum extrusion coating and coil coating with long guaranteed life and reduces gloss at all viewing angles. It is gaining use in high solid pigmented metal office furniture finish [44].

Fire extinguishing powders

Precipitated silica ensures extremely good humidity protection due to its hygroscopic nature, so extinguishers remain fully operational even after extended storage [44].

2.4.2 Rubber grade precipitated silica

Rubber application is expected to witness substantial growth among other applications, growing at a CAGR of over 7.2% of the overall volume share from 2015 to 2022. Increasing application scope of the compound in manufacturing conveyor belts, transmission belts, rice rollers, PVC sheets, thermoplastic rubbers, shoe soles, and silicon tubes are expected to have a positive impact on precipitated silica market growth. Growing green tire applications on account of its benefits offered such as optimized fuel consumption and reduced rolling resistance is expected to propel the market demand [43].

Adhesive

Precipitated silica is useful to enhance bond strength and as a reinforcing and thickening agent [44]. The dispersed silica particles within a liquid adhesive harden fast when it is in contact with solid surface, in both natural and synthetic rubber-based adhesive. Silica provides thixotropy, reinforcement and promotes adhesion as well as serves as extenders;

therefore, it raises quality and lowers cost. It is also used to adjust rheology and provide reinforcement.

Silica prevents resin separation and the settling of pigments and heavy fillers [44]. It prevents excessive penetration of adhesive into porous adherents. It improves flow control and heat resistance of hot melts in application.

It serves as a free-flowing agent for spray dried resins [44]. Fig. 2.10 shows the different uses of adhesive.



Fig. 2.10 Different uses of precipitated silica as adhesive.

Shoe soles

Precipitated silica is used in shoe soles for its resistance to wear and tear, its non-scuffing characteristics and to obtain compounds with light color or even transparent materials. It provides superior durability and resilience and improved modulus. Precipitated Silica provides superior durability and resilience while improving compound stiffness for all types of rubber soled footwear [44].



Fig. 2.11 Precipitated silica is used in all types of rubber soled footwear.

Conveyor belt and transmission belt

Precipitated silica is used to improve the tear strength due to its small particle size and complex aggregate structure [45]. It imparts the highest degree of reinforcement to elastomer compounds. Precipitated silica is used to prevent from cracking and cut growth of conveyor belts and power transmission belts.

- Provides higher tensile strength
- Provides longer life and durability
- Imparts abrasion resistance
- Improves tear resistance



Fig. 2.12 Precipitated silica is used to improve strength of rubber belts.

PVC sheets

Precipitated silica is used to improve pigment dispersion and acts as a parting agent and as an absorbent to improve the flow and imparts a dry feel to the compound.

- Improves tear resistance
- Acts as reinforcing agent
- Provides higher tensile strength
- Provides longer life and durability



Fig. 2.13 Precipitated silica is used to improve pigment dispersion and act as a pairing agent in PVC sheets.

Railway pads

Precipitated silica is used in railway pads for the following reasons:

- Provides increased abrasion resistance and strength
- Provides superior durability and resilience and improved modulus



Fig. 2.14 Precipitated silica is used to increase abrasion properties and durability of railway pads.

Rice rollers and rubber rollers

Precipitated silica is used in rubber rollers and rice rollers for following reasons:

- Improves the abrasion resistance and stiffness
- Improves tear resistance
- Acts as reinforcing agent
- Provides higher tensile strength
- Provides longer life and durability



Fig. 2.15 Rice rollers and rubber rollers.

Rubber products and rubber hoses

In industrial rubber, precipitated silica confers superior strength and durability on industrial rubber belts and rubber hoses together with improved heat resistance and tear strength. It also improves adhesion in wire and fabric coat compounds and allows for rapid and easy processing, resulting in smooth finished surfaces in molded products [44].



Fig. 2.16 Rubber products and rubber hoses.

Silicon tubes

Silicon rubber is used in a number of applications where its unique properties provide a substantial benefit. Many of these properties are highly dependent on the type and quantity of filler used in the compound. Particular silicon rubber applications have certain physical strength requirements, for example wire and cable, medical and surgical, belting, hose, tubing and various fuel-resistant rubbers uses. When physical strength is a primary concern, reinforcing silica is the filler of choice [44].

Precipitated Silica is used in Silicon Rubber for following reasons:

- Improves process ability of raw mixture
- Offers resistance to heat aging
- Minimizes craze hardening
- Provides superior resilience and compression set



Fig. 2.17 Silicon tubes.

Rubber and solid tires

Precipitated Silica is used in tire industry to improve the tear resistance of truck and heavy equipment tires and also to enhance adhesion between the metallic reinforcement and the rubber of radial tires [45,46]. Nowadays, use of precipitated silica have been extended to passenger car tires as well.

Precipitated Silica is also used in “Green Tires” due to excellent dispersion capacity and low rolling resistance and improves their longevity and adherence.



Fig. 2.18 Rubber and solid tires.

Textile cots and aprons

Precipitated silica is used for reinforcing silica for textile cots and Aprons.



Fig. 2.19 Textile cots and aprons.

CHAPTER THREE
EXPERIMENTAL METHODOLOGY

3. EXPERIMENTAL METHODOLOGY

3.1 Introduction

In order to produce precipitated silica by using chemical extraction and precipitation method, several precautions must be taken into considerations. The appropriate methodology has significant impact for conducting experimental research so that the most accurate results can be obtained and optimum parameters can be found.

In chemical precipitation method of producing precipitated silica, a solid form from a liquid due to a chemical reaction. Precipitated silica is formed by mixing of solutions of sodium silicate with sulphuric acid in water. A chemical reaction occurs, and pellets of pure silica form. The physical properties of the resulting silica can vary slightly depending on the exact conditions under which the precipitation reaction takes place. Changes in temperature, concentration of the solution used, and the ratio of the ingredients in the mixture can all alter the physical properties of the silica particles.

After the silica has formed, it is separated from the solution, cleaned and dried. This involves washing the silica to remove all traces of chemical salts and insoluble impurities of the precipitation process. The washing and drying process can also affect the characteristics of the particles. Particles size, porosity and density can all be manipulated this way to some extent.

This chapter elaborates the experimental approach followed throughout this research work from the pretreatment method until the characterization of the rice husk ash and precipitated silica.

3.2 Schematic Representation of Research Work

Silica has been obtained by alkali extraction of rice husk ash in presence of sodium hydroxide (NaOH) at 120-170°C temperature, while kept pressure at 1-8 atm. Silica extracted as sodium silicate and then precipitate using sulphuric acid. Afterwards, it was dried and milled. Fig. 3.1 shows the schematic diagram of the research work to produce precipitated silica from rice husk ash.

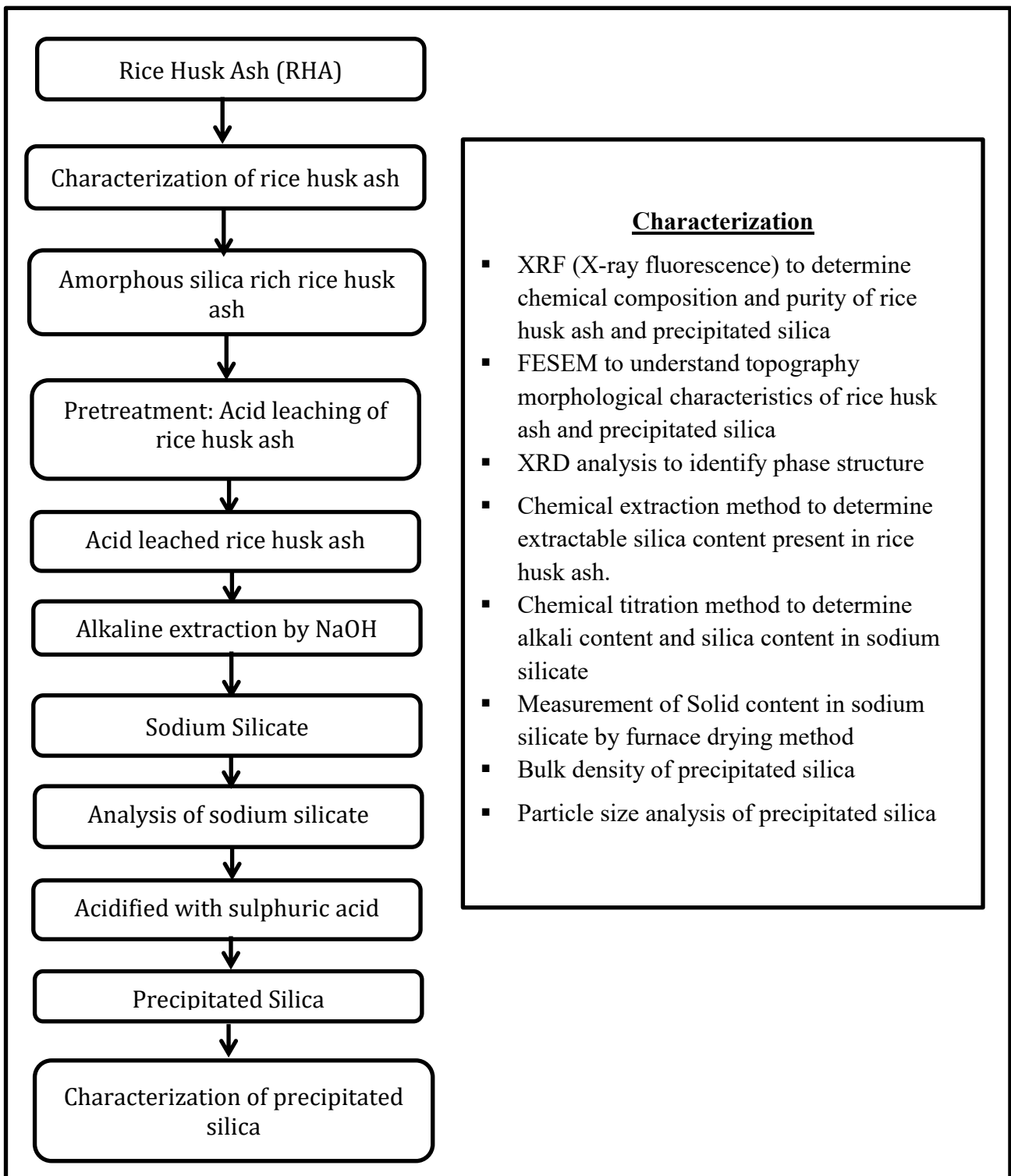


Fig. 3.1 Schematic diagram of the research work.

The materials required for this research includes:

- Rice husk ash (RHA)
- Caustic soda flakes (Sodium Hydroxide - NaOH)
- Commercial grade hydrochloric acid (HCl)
- Commercial grade sulphuric acid (H₂SO₄)

3.3 Rice husk ash (RHA)

The rice husk ash as main silica source, used in this research, was collected from different rice mills of different areas stated in following table. The rice mills currently dispose the rice husk ash in open environment which creates environment pollution. Quality of rice husk ash is completely depending on the design of the boiler. By reviewing literatures, high purity amorphous silica contain rice husk ash can be obtained from fluidized bed combustion system at 700-800°C.

Rice husk ash has no commercial value. So, the cost includes labor cost and delivery cost. If rice husk ash is collected from own FBC boiler (fuel: Rice Husk) used in the production of precipitated silica, it adds negligible cost on the production cost.

Table 3.1: Rice husk ash collected from various rice mills in Bangladesh

Sl. No.	Rice Mill Zone	Design of Boiler	Percentage of Silica	No. of Sample
1.	Mymensingh, Dinajpur and Rajshahi zone	Fluidized bed combustion (FBC) boiler	95-97%	3 nos.
2.	Sherpur zone	FBC and Reciprocating boiler	85-90%	1 no.
3.	Natore and Bogura	Do	85-90%	2 nos.
4.	Comilla zone	Chain grate stoker boiler	80-85%	1 no.
5.	Brahmanbaria zone	Do	80-85%	1 no.

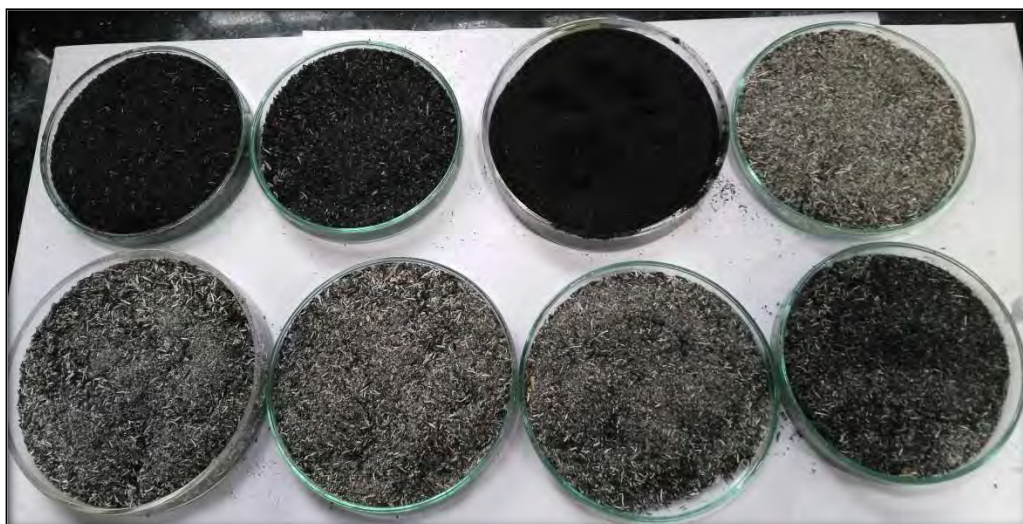


Fig. 3.2 Rice husk ash as-received collected from various rice mills.

3.4 Other Chemicals

Among chemicals used in this study include HCl, NaOH and H₂SO₄. All chemicals were used as received without any purification.

Table 3.2: Summary of chemical used in this process

Sl. No.	Name of the chemicals	Source	Specification	Function
1.	Hydrochloric acid, HCl	Samuda Chemicals	Commercial grade: 32-33% purity	For acid leaching of rice husk ash
2.	Caustic soda flakes, NaOH	Samuda chemicals	Commercial grade: 98-98.5% purity	For alkaline extraction of rice husk ash
3.	Sulphuric acid, H ₂ SO ₄	TSP Super Complex	Commercial grade: 96% purity	Neutralization of sodium silicate

3.4.1 Commercial grade caustic soda flakes (NaOH)

Caustic soda flakes were used as the alkali (sodium oxide-Na₂O) source to extract amorphous silica from rice husk ash. It was collected obtained from local manufacturers. Furnace method of sand process use sodium carbonate as their alkali source which is 100% imported from foreign country. Price of Commercial grade caustic soda flakes is around 40-45 Tk per kg in Bangladesh.

3.4.2 Commercial grade hydrochloric acid (HCl)

Hydrochloric acid was used to remove the metal impurities from rice husk ash by acid leaching treatment. Hydrochloric acid was collected from local manufacturers. It's a very low-cost product as 5-6 Tk per liter of commercial grade hydrochloric acid.

3.4.3 Commercial grade sulphuric acid (H₂SO₄)

Sulphuric acid was used to precipitate the silica from sodium silicate solution produced from alkaline extraction of rice husk ash by acid precipitation method. Sulphuric acid was collected from local manufacturers. It's a low-cost product as 13-15 Tk per liter of commercial grade sulphuric acid.

3.5 Chemical Reagents

The reagents used in this research are given in table below.

Table 3.3: Summary of reagents used in this research

Sl. No.	Name of the reagents	Purity	Functional area
1.	Sodium hydroxide pellets	99%	Determination of silica content in rice husk ash
2.	Lab grade HCl	37%	Determination of alkali content by chemical titration
3.	Sodium carbonate anhydrous	99%	Standardization of hydrochloric acid solution
4.	Methyl orange	99%	Indicator
5.	Silver nitrate	-	To check chloride impurities
6.	Nitric acid		
7.	Barium chloride	-	To check sulphate impurities
8.	Hydrofluoric acid	-	Determination of purity of silica

3.6 Equipment and Instrument

The lab equipment used in the research work includes:

- Glass beaker
- Conical flask
- Bottle neck kettle
- Electronic weighing balance
- Hotplate magnetic stirrer
- Nickel crucible
- Vacuum filtration system
- Pressure vessel
- Muffle furnace
- Hot air oven
- Desiccators
- Platinum crucible

3.7 Characterization Techniques

The bulk of the received rice husk ash, sodium silicate after alkali extraction and desired product precipitated silica having high purity by acid neutralization was characterized by FESEM for topography and morphological information, XRF for determine chemical composition and XRD for determine phase structure.

Table 3.4: Summary of characterization equipment

Sl. No.	Name of the apparatus	Specification
1.	FESEM	JEOL JSM-7000F FESEM With Schottky field emission gun
2.	XRF	LAB CENTER XRF -1800 250 μm mapping for wavelength dispersive analysis; 4 kw thin window X-ray tube
3.	XRD	Empyrean XRD by PANalytical (Netherlands)

3.8 Experimental Methods

In this new process, precipitated silica is manufactured by using rice husk ash as a source of silica and this ash (as-received) was then reacted with sodium hydroxide which yields the sodium silicate, which on further reacting with sulphuric acid gives precipitated silica along with by-product sodium sulphate. The basis of advantages of this proposed process is first the rice husk ash with higher amorphous silica content. The process to extracts all the silica contents from the rice husk is just by burning the rice husk under controlled conditions of air and temp, which is conducted in fluidized bed furnace and by this condition we can get the clear white ash in the furnace. The basic steps in the production of precipitated silica are,

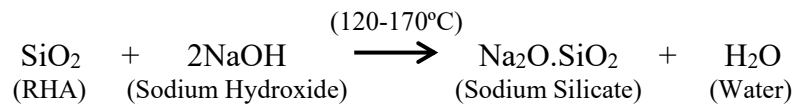
- Characterization of rice husk ash to select suitable rice husk ash for maximum productivity
- Acid leaching treatment of rice husk ash to remove metal impurities
- Dissolution of amorphous silica of rice husk ash in alkaline solution at specified temperature and pressure
- Separation of solid carbon residue from diluted sodium silicate solution using advance filtration technique named pre-filter.
- Precipitation of silica from sodium silicate solution using acid at specified temperature

- Removal of sodium sulphate produced in acid precipitation stage as by-product by hot water washing method.
- Aging at specific temperature to get desired surface area.
- Drying at 110°C
- Pulverizing and sieving to get desired particle size.

The following two reactions are mainly described the process.

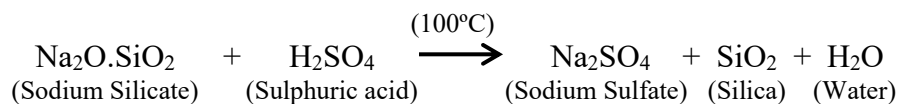
3.8.1 Alkaline extraction of rice husk ash

The amorphous silica content of rice husk ash is reacted with alkali content of sodium hydroxide to extract silica in the form of sodium silicate at 120-170°C. Yield of silica is completely depending on temperature.



3.8.2 Precipitation of silica

The silica content of sodium silicate is then precipitated by neutralizing sodium silicate solution using sulphuric acid. Reaction can occur at room temperature but to get desired properties, boiling temperature is introduced.



3.9 Characterization of Rice Husk Ash by Analytical Methods

The samples of rice husk ash were collected from the local auto rice mills in 1st half of year in 2014. The collected raw material rice husk ash was analyzed for investigating the following properties:

- Moisture content of rice husk ash by oven drying method
- Extractable amorphous silica content in rice husk ash using alkaline extraction of the ash.
- Loss on ignition (LOI) was carried out by igniting the sample at 950°C for 2 hours.

3.9.1 Determination of moisture content of rice husk ash

The moisture content of the rice husk ash was determined by the drying oven method. A petri dish was cleaned and dried at 110°C for 1 hour. After 1-hour, dry hot petri dish was cooled in desiccator for 15 min and the empty petri dish was weighed and recorded. Raw materials were taken with a spatula into the dried petri-dish and the combined weight was recorded. Materials should be taken in such a way that its weight lie between 1.5 and 3 gm. After weighing, the open petri-dish was placed inside an electrical hot air oven capable of maintaining temperatures between $110 \pm 2^\circ\text{C}$. Petri-dish containing samples were kept in the oven for 4 hours. At the end of the drying period, petri-dish was closed with its cover and with the help of a pair of tongs, was transferred into desiccators where the samples were allowed to cool to room temperature. Finally, the weight of the petri-dish containing the oven-dried sample was taken. This procedure was repeated three times for each sample and average moisture content was reported as a percentage with two decimal places mentioning the basis used in the calculation.

Calculation

Weight of sample = (Weight of sample + petri-dish) – Weight of petri-dish

Weight of moisture = (Weight of dry sample + petri-dish) – (Weight of sample + petri-dish)

$$\therefore \text{Moisture content (MC)} = \frac{\text{Weight of moisture}}{\text{Weight of sample}} \times 100 \%$$

3.9.2 Determination of silica content present in rice husk ash

10 gm rice husk ash and 150 ml de-ionized water were weighed and transferred into a glass beaker. 10 gm sodium hydroxide was added to the rice husk ash slurry. The mixture was agitated and heated at 100°C for 4 hours using hot plate magnetic stirrer. Makeup water was regularly added to keep the water level constant. An oven-dried nickel crucible was cooled in a desiccator for 15 min and then the empty weight of cooled crucible was weighed and recorded. The rice husk ash slurry solution was then filtered through dried crucible under vacuum. The carbon residue was washed with hot water to remove the silicate.

The crucible with carbon residue was dried at 110°C for 4 hours in hot air oven. Then, the dried crucible with carbon residue was weighed and recorded.

Weight of extractable silica = Weight of rice husk ash - (Weight of dry crucible with residue - Weight of dry crucible before filtration)

Calculation:

$$\text{Silica \%} = \frac{\text{Weight of extractable silica}}{\text{Weight of rice husk ash taken}} \times 100\%$$

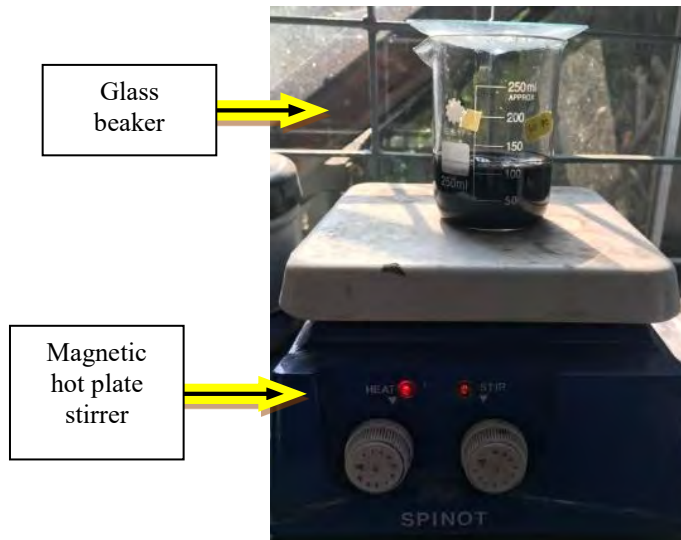


Fig. 3.3 Determination of silica content in rice husk ash.

3.9.3 Determination of residual carbon content in rice husk ash through loss on ignition (LOI) test

The residual carbon content in the rice husk ash samples were determined via loss on ignition (LOI) analysis. 5 gm oven dried ash sample at 110°C was subjected to a temperature of 950°C in a muffle furnace for two hours or until no further weight loss was observed. The residual carbon content in the ash is given by the mass loss between the initial and final ash sample. Ash samples containing mostly carbon (i.e. mostly black) were subjected to proximate analysis to determine the total amount of combustible matters (volatile matters and fixed carbon).

The amount of fixed carbon is obtained through the differential method:

$$\text{Fixed carbon (dry wt\%)} = 100\% - \{\text{volatile matter (dry wt\%)} + \text{ash (dry wt\%)}\}$$

3.10 Removal of Metal Impurities by Acid Leaching

Several kinds of acids, both mineral and organic, have been reported to be used for pretreat rice husk before other value adding processes such as incineration begin [30,47-51]. However, HCl has proved to be most effective in removing metallic impurities from the husk and rice husk ash and so it is by far the most widely used [49,52,53]. Chakraverty et al. [54,55] found that leaching of rice husk ash in 1N HCl is effective in removing most of the metallic impurities. Other researchers [49] used organic acids and compared results with those obtained by using other different mineral acids in pretreating rice husk and its ash concluded that HCl is better. Their order of efficiency is $\text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3$. However, Umeda and Kondo [56] reported a very high purity (>99.5%) silica from rice husk ash on pre-leaching it with citric acid.

While acid leaching affects the chemical composition of the husk, it does not affect the structure, whether crystalline or amorphous of the silica. Thus, the change of phase from amorphous to crystalline is not affected by the pretreatment method employed. An insight into these dynamics was presented in the research report of Real and coworkers [51].

Other acids such as H_2SO_4 , HNO_3 and their mixture, have also been used in the acid pretreatment [31,47,50,54,57]. The general leaching effects of H_2SO_4 , HNO_3 and HCl are similar, but HCl is superior to H_2SO_4 and HNO_3 in removing the metallic ingredients [54]. Some researchers [30,50] also attempted chemical post treatment of incinerated rice husk using HCl but the results were inferior to those of the pretreatment.

Acid leaching of the rice husk ash was carried out to remove soluble elemental impurities and hence increase the purity of the silica content. Leaching was carried out in 1-5% HCl. The HCl solution was prepared from a standard HCl stock of mean concentration 37 wt% and density 1.19 g/mL.

The leaching reactor was 5L round bottom neck glass reactor with rubber cork. Three top ports are designed to accommodate a separator funnel to charge rice husk ash and diluted acid solution; as well as condenser for reflux and a two teflon coated blade glass stirrer. The port for the separator funnel works for two purpose such as sampling port and temperature probe port. The experimental set up for leaching is shown in Fig. 3.4

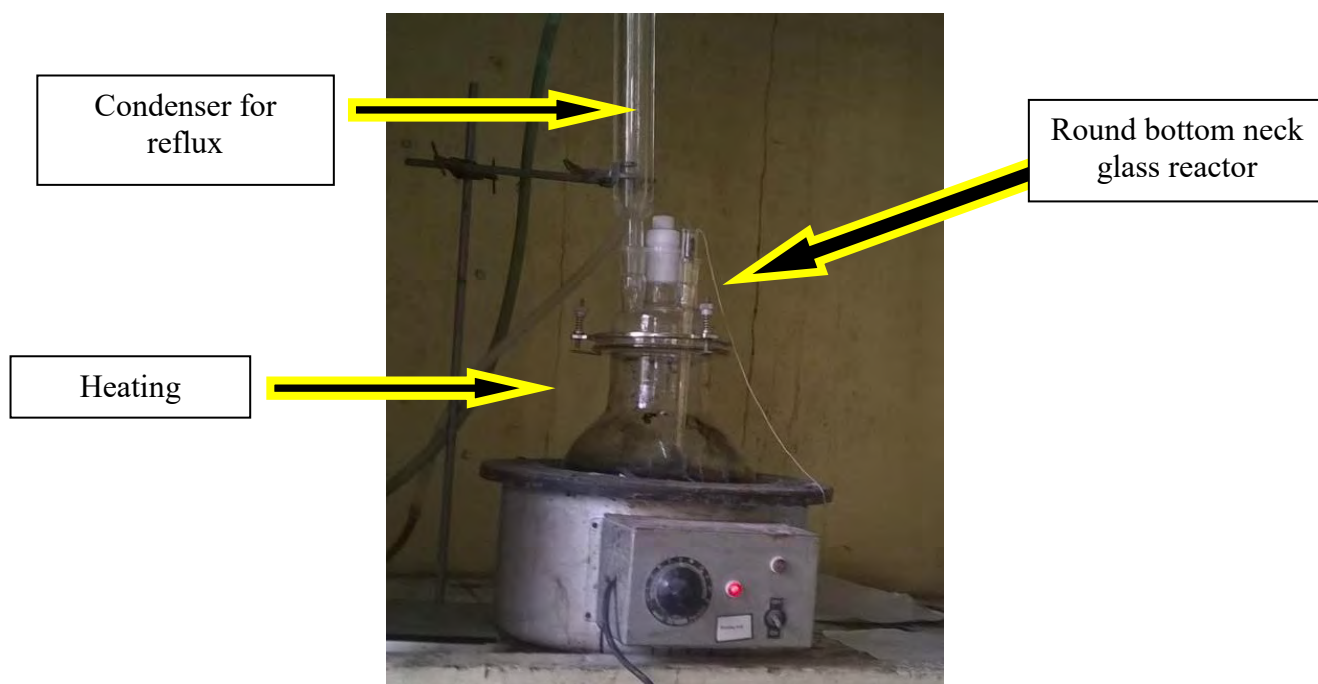


Fig. 3.4 The experimental set-up for acid leaching treatment of rice husk ash.

Leaching treatment was carried out by charging about 1000 gm rice husk ash and 4000 ml of HCl solution into reactor and refluxed at 100°C for 1-3 hours. Leaching time was varied between 1-3 hrs and the temperature was varied between room temperature and 100°C with continuous stirring at 600 rpm. Vacuum assisted filtration was used to separate the residue (washed rice husk ash) and supernatant liquid.

The rice husk ash residue was thoroughly washed with hot water followed by de-ionized water till it is acid free as indicated by pH paper (pH 6-7). Samples of the dry residue (acid-treated rice husk ash) were then prepared for alkali extraction to make sodium silicate.

3.10.1 Extraction of silica by alkaline extraction of rice husk ash

Before starting the alkaline extraction process, the raw materials were prepared according to the following procedures:

Preparation of slurry mixture of rice husk ash and Water

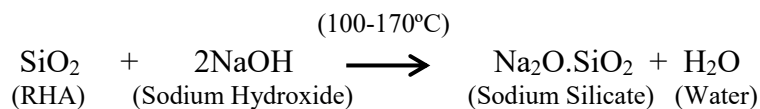
The required quantity of acid treated rice husk ash (Approx. 1 kg dry basis) is mixed with iron-free water (ratio varying from 1:5 to 1:10 with respect to dry ash) and agitated the solution for 15 mins to get flow-able slurry mixture.

Preparation of sodium hydroxide solution for digestion

The required quantity of Sodium Hydroxide (ratio varying from 1:2.5 to 1:3.3 with respect to dry ash) is dissolved in similar quantity of water and agitated the solution for 15 mins to dissolve the caustic soda flakes completely into water.

Digestion of rice husk ash with sodium hydroxide

The main step is extraction of silica from ash as sodium silicate using sodium hydroxide. This reaction is carried out at temperature in the range 100°C-170°C and pressure ranging from 1-8 atmospheres. High reaction temperature and pressure can be avoided if rice husk ash is obtained by burning rice husk at 650-700°C in FBC boiler. This ash is mostly amorphous silica which is reactive around 100°C with NaOH solution at atmospheric pressure to yield sodium silicate. But considering economical point of view, high temperature (120-170°C) was selected to reduce the consumption of sodium hydroxide.



A viscous, transparent, colorless sodium silicate solution (~15%w/w) is obtained after filtration of the reacted slurry (consisting of residue undigested ash, sodium silicate, water).



Fig. 3.5 Alkali extraction in laboratory glass beaker and in pilot digester.

The following reaction parameters are controlled to optimize the reaction:

- Ratio of rice husk ash and sodium hydroxide (1:2.0 – 1:3.3)
- Ratio of rice husk ash and water (1:5 – 1:10)
- Molarity of sodium hydroxide solution (0.75 – 1.50)
- Reaction period (2-4 hrs)
- Reaction temperature (120-170°C)

Separation of carbon residue by filtration

Laboratory filtration system with vacuum pump was used to separate the residue and diluted sodium silicate liquid. The residue was thoroughly washed with tap water followed by de-ionized water till it is alkali free as indicated by pH paper (pH 6-7). The residue obtained was oven dried to constant weight at 105°C. This residue is called activated carbon.

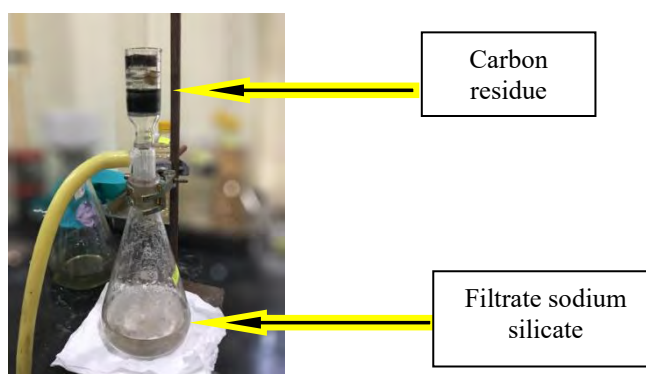


Fig. 3.6 Separation of carbon residue by filtration in lab.

3.11 Analytical Methods of Checking the Properties of Alkaline Silicate

3.11.1 Specific Gravity of alkaline silicate solution

Specific gravity and density can be determined by the same hydrometer (used for liquid which is heavier than water). The material to be tested was poured into a clean hydrometer jar, the diameter of which should be at least 2.5 cm greater than the diameter of the hydrometer (figure 3.7) used. All the air bubbles were removed that formed in the liquid. The jar was kept in a vertical position and lower down the hydrometer gently into the material. The point was read to which the sample rises, with the eye-placed at the principle surface of the material. This reading was the specific gravity as well as density of the material under test. Fig. 3.8 shows the density test by hydrometer.

$$\text{Specific Gravity (SG)} = 145 / (145 - \text{Density in Baume degree})$$



Fig. 3.7 Hydrometer.



Fig. 3.8 Density was tested by deeping the hydrometer in the liquid.

3.11.2 Soluble silicate content of diluted alkaline silicate solution

The soluble silicate content of water glass solution was determined by furnace method. A sample of known mass was taken in a pre-weighted dry nickel crucible. The nickel crucible with sample was then placed in pre-heated muffle furnace at 500°C and kept it in the furnace for 1 hour. The hot nickel crucible with dry sample was placed in desiccator for cooling. The cooled nickel crucible was weighted and quantified for the determination of the solid content of the sample. The solid content was determined by mass balance using following formula,

$$\text{Total soluble silicate (wt. \%)} = (\text{Wt. of dry sample} / \text{Wt. of liquid sample taken}) \times 100$$



Fig. 3.9 Nickel crucible in muffle furnace.

3.11.3 Alkalinity of alkaline silicate solution

The principle of the method is based on titration of the total alkalinity of a test portion with a standard volumetric solution of hydrochloric acid in the presence of methyl orange as indicator.

Procedure: A liquid sample of water glass of known mass was weighed and placed the test portion in a 250-ml volumetric flask and dissolved with water. Few drops of methyl orange solution were added to the test sample. Titration was made with the standard volumetric hydrochloric acid solution until the indicator changes from yellow to orange-pink. The total alkalinity, expressed as a percentage by mass of sodium oxide was determined by the given formula:

$$\text{Alkalinity} = 3.1 \times (\text{volume of HCl used in the titration} / \text{Weight of sample})$$

3.11.4 Silica content of alkaline silicate solution

From alkaline silicate solution obtained in the filtration stage as filtrate, a sample of known mass was taken and was added hydrochloric acid until it reaching pH 7.0. In this pH the silica precipitates, also resulting a salt, the sodium sulfate (Na_2SO_4). The removal of sodium sulfate was made using boiling distilled water by vacuum filtration. The process resultant silica gel was placed to dry at 120°C for 8 hours, weighed and quantified for the determination of the silica content converted to silicate, in function of the amount of silica contained in the rice husk ash. The silica conversion by acid neutralization method was determined by mass balance using following formula,

$$\text{SiO}_2 \text{ precipitation (wt. \%)} = (\text{Wt. of dry precipitated silica} / \text{Wt. of water glass}) \times 100$$

3.11.5 Molar Ratio of soluble silica to alkali

The ratio of total soluble silica to total alkalinity was calculated by following given formula:

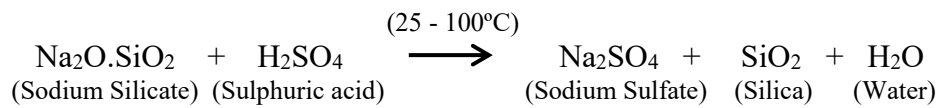
$$\text{Molar Ratio} = \text{total soluble silica content (wt\%)} / \text{total alkalinity (wt\%)}$$

3.12 Precipitation of Silica from Sodium Silicate

In this step of the process, silica is precipitated from sodium silicate using sulphuric acid. This is the crucial step to obtain the precipitated silica of required specifications by varying the parameters. This step requires controlled conditions of addition rate of sulphuric acid and

temperature of reacting mass in a neutralizer. The temperature is in the range of room temperature to 100°C and pressure is the normal atmospheric pressure.

The reaction is as follows:



Various silica concentrations in sodium silicate solution ranging from 2.5% to 10 % were tried for precipitation. The variation of parameters results in silica of different quality. It was observed that silica concentration in the range of 4.5% to 6.0% were suitable for producing the silica required by most of the industries. Higher and lower silica concentration than the above range produced silica of higher density, in addition to the difficulties in handling the slurry during precipitation at higher concentrations. Precipitation was carried out at various temperatures and it was observed that lower temperatures produces gel like silica with high density.

Purification of this silica for removal of sulphate impurities constitutes the third step of process. For this successive demineralized water washings are given in the filter process itself. The conductivity of the effluent follows a decreasing trend owing to removal of sodium sulphate. Thus, conductivity can be used as the criteria to decide the number of washings for obtaining silica of desired purity. Silica after removal of sulphates (wet silica) is generally spray dried to obtain the amorphous powder form in the final step of the process. The purification and drying produce silica in white amorphous powder form. Sodium sulphate from the effluent water and good quality bricks from ash residue are other recoveries.

3.12.1 Preparation of sulphuric acid solution

500 ml Dilute sulphuric acid solution having specific gravity 1.1–1.3 g/ml was prepared by adding 50 ml of concentrated sulphuric acid to 450 ml of water in a beaker with constant stirring with cooling.

3.12.2 Preparation of sodium silicate solution

Diluted sodium silicate solution having specific gravity 1.15-1.20 g/ml was collected from previous stage of alkaline extraction of rice husk ash.

3.12.3 Acidification of alkaline silicate solution

Diluted sulphuric acid solution was transferred into beaker and started agitation with laboratory stirrer. Sodium silicate stock solution was added drop wise by a separating funnel or a burette with continuous stirring till gel point as indicated by solidification was obtained. A minimum quantity of water was added to make the gel homogeneous so that it can be stirred with ease. The slurry solution was then stirred for 30 minutes.

The acidification of sodium silicate solution was done very slowly (otherwise chemistry of reacting mass may change along with physical properties/form) until acidic conditions are reached. The acidic conditions indicate approximately complete precipitation of silica from sodium silicate. A white precipitate of silica in solution of sodium sulphate is obtained.

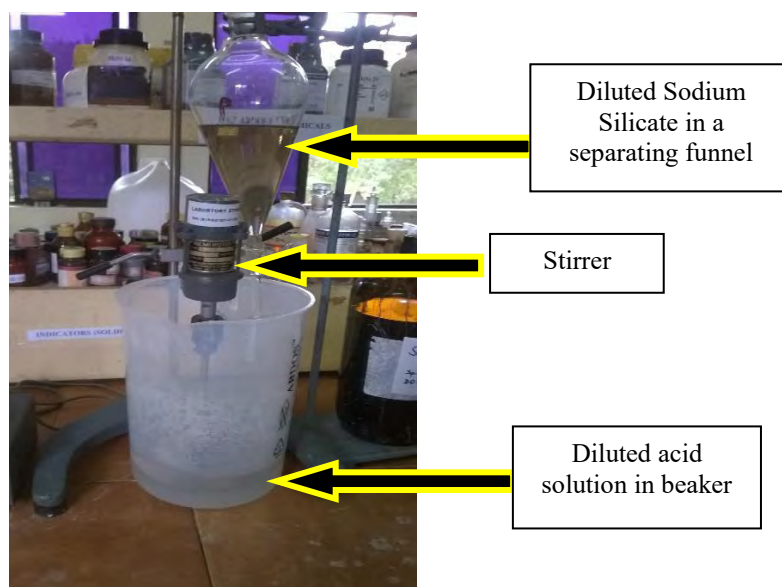


Fig. 3.10 Acidification of alkaline solution.

3.12.4 Separation of precipitated silica by vacuum filtration

The formed gel was then filtered by using gentle suction and an ordinary filter cloth on a Buchner funnel. Purification of this silica for removal of sulphate impurities constitutes the third step of the process. For this successive demineralized water washings are given in the filter press itself. The conductivity of the effluent follows a decreasing trend owing to removal of sodium sulphate. Thus, conductivity can be used as the criteria to decide the number of washings for obtaining silica as desired purity.



Fig. 3.11 (a) Separation of silica by filtration; (b) Wet precipitated silica after filtration.

3.12.5 Purification of precipitated silica by removing sodium sulphate

Washing and purification of the precipitate is carried out to remove the soluble contaminants from the precipitate. Usually a dilute solution of a strong electrolyte having a common ion with the precipitate is employed for washing precipitates to reduce errors due to solubility and loss of precipitate. In this research, 10% of barium chloride solution was used with distilled water for rinsing to remove trace amount of sodium sulfate contain in gel.



Fig. 3.12 (a) Formation of transparent gel solution; (b) Transparent solid gel after filtration.

3.12.6 Aging and Drying

Aging was important to get high surface area of silica. Aging temperature was varying from room temperature to 70°C. Heat treatment of the washed precipitate may be simple drying of the precipitate collected over a sintered glass crucible or Petri dish or aluminium foil paper at 105 – 120°C in a hot air oven or a strong heat treatment to decompose the precipitate thermally to yield a final product of definite stoichiometry. The wet precipitated silica was dried kept in a hot air oven at 105 – 120°C till the dry material get it constant weight.

3.12.7 Pulverizing

Silica after drying was milled to obtain the fine and free flow amorphous powder with specific bulk density. The prepared silica powder is then stored in an air tight container.



Fig. 3.13 Precipitated silica powder after drying and milling.

3.12.8 Associated recoveries

The other associate recovery is sodium sulphate. Effluent wash water obtained after washing precipitated silica (wet impure silica) contains sodium sulphate. By evaporation of water in multiple effect evaporators, followed by crystallization, filtration and drying, crystals of sodium sulphate can be obtained. The residue ash in sodium silicate production can be utilized for making good quality bricks. Retained sodium silicate in residue ash acts as a binder and with incorporation of suitable ingredients high quality bricks can be manufactured.

3.13 Analytical Methods for Checking the Quality of Precipitated Silica

3.13.1 Determination of purity of precipitated silica

Reagents

- Concentrated Hydrochloric Acid - Density 1.18 g/ml.
- Hydrofluoric Acid - 40 percent.
- Concentrated Sulphuric Acid - Density 1.84 g/ml.

Procedure

The sample was first dried to constant mass at $105 \pm 2^\circ\text{C}$. Weighed about 0.5 gm, nearest to 0.001 gm (M), in a clean and dry porcelain dish and carefully moistened it with distilled water. Added slowly 25 ml concentrated hydrochloric acid and 10 ml distilled water and evaporated to dryness. This treatment was repeated twice, each time with an addition of 15 ml concentrated

hydrochloric acid and some distilled water. The entire dried contents of the dish were then transferred with 15 ml concentrated hydrochloric acid and about 150 ml distilled water into a beaker, and heated with continuous stirring, but not up to boiling. The left-over silica was filtered through an ashless filter paper (whatman filter paper-42) and washed repeatedly with hot water until neutral. The filtrate and the washings were collected and, if necessary, used for further analysis. The filter paper with the silica was carefully ashed in a platinum crucible and the residue was kept for 20 minutes at about 900°C. Cooled and weighed to nearest 0.001 gm (M1). To the contents of the crucible, added a little distilled water, 5 drops of concentrated sulphuric acid, and 15 ml of hydrofluoric acid. Under careful heating, and slow rise of temperature, the contents of the crucible were dried. This step is repeated two more times. The residue is then heated to red-heat for 5 minutes at 1000°C, and after cooling to room temperature in a desiccator, weighed accurately to 0.001 gm (M2).

Calculation

The content of SiO₂ in percentage is percentage SiO₂ = $\{(M1 - M2)/M\} \times 100$

Where

M1 = mass in gm before the treatment with hydrofluoric acid,

M2 = mass in gm after treatment with hydrofluoric acid, and

M = mass in gm of sample.

3.13.2 Specific gravity of sodium silicate solution

Around 60-70 ml of the solution was transferred into a density cylinder or 100 ml measuring cylinder. A hydrometer (heavier than water) of specific gravity range 1.00 to 2.00 and noted down the specific gravity value.

3.13.3 Presence of chlorides

Materials Needed for the Test

- Distilled or deionized water.
- Test tube, rinsed in distilled water.
- Dilute (5%) nitric acid, in a dropper bottle.
- Silver nitrate test solution, in a dropper bottle.
- Black or dark background with a strong side light.

Preparation of silver nitrate solution:

To make test solution dissolve 1.7 gm of silver nitrate crystals into 98 ml of distilled water. Store the solution in a dropper bottle in a dim or dark place, because it is somewhat light sensitive.

Procedure

- Placed a sample of the washed water (5 to 10 ml) in the clean test tube. Added one or two drops of dilute nitric acid. Shaked to mix. If the solution fizzes, continue to add acid until the fizz stops. Hold the test tube up to a strong side light with a dark area behind the test tube.
- Added two drops of the silver nitrate solution. Observed the sample closely. The formation of a white precipitate (i.e., a cloudiness) indicates the presence of chlorides. Further washing of silica is required to remove chlorides completely.

3.13.4 Presence of sulphates

Materials Needed for the Test

- Distilled or deionized water.
- Test tube, rinsed in distilled water.
- Hydrochloric acid
- 10% barium chloride solution, in a dropper bottle.

Procedure

Collected ~5-10 ml of washing water in a test tube, added 1-2 drops hydrochloric acid followed by 4-5 drops barium chloride solution. Absence of white precipitates indicated the washing water was free of sulphates.

3.13.5 Determination of pH

Procedure - Weighed about 5 g of the material and transfer it to a 500-ml beaker. Add 100 ml of freshly boiled and cooled distilled water. Allowed to stand for 30 minutes with occasional stirring. Filtered and rejected the first 50 ml of the filtrate and collected the remaining filtrate in a breaker. Determined the pH of the solution by means of a suitable pH meter using glass electrodes.

3.13.6 Moisture content

Procedure: Weighed accurately about 10 g of the material and heat in a weighted empty weighing bottle at 105°C for 2 hours. Cooled and weighed till a constant mass was obtained.

Calculation

Moisture content = (loss in mass in gm / mass in gm of the material taken for the test) x 100

3.13.7 Loss on Ignition (LOI)

Procedure - Weighed accurately about 1 g of the material as dried in a silica or platinum crucible. Ignited at 900°C for 2 hours. Cooled and weighed till constant mass is obtained.

Calculation

LOI, % = (loss in mass in gm / mass in gm of the material taken for the test) x 100

3.13.8 Bulk density

Procedure: Transferred the powder to 25 ml mark into a dry 25 ml plastic measuring cylinder with lid. Closed the lid and dropped the cylinder on to a rubber pad from a height of 5 cm. Recorded the volume of powder (V). transferred the powder into a tared crucible dish and found the weight of the powder (W).

Calculation

$$\text{Bulk density, gm/ml} = W/V$$

3.13.9 Determination of size distribution of particles through sieve analysis

The size distributions of particles used in this study (sand, rice husk and rice husk) were determined by means of sieve analysis. Sieving tests were carried out in a sieve shaker. A sufficient amount of particles was sieved for approximately 30 minutes. The particles (powder sample) were sieved into five size ranges: 600 mesh, 400 mesh, 325 mesh, 200 mesh and 100 mesh. The particles (large particle) were sieved into five size ranges: 0.5 mm-1mm-2mm-2.8mm-4.75mm sieve.

3.14 Summary of Characterization of Raw Materials and Products

The characterization section is mainly divided into two categories as follows:

- Characterization of research material – rice husk ash
- Characterization of research output – sodium silicate, precipitated silica and carbon residue

3.14.1 Characterization of rice husk ash

The collected raw material rice husk ash was analyzed for investigating the following properties:

- Chemical composition of rice husk ash using XRF
- Extractable amorphous silica content in rice husk ash using alkaline extraction of the ash.
- Moisture content of rice husk ash by oven drying method
- Loss on ignition (LOI) was carried out by igniting the sample at 950°C for 2 hours.
- Crystal phases of rice husk ash using XRD
- Topography and morphological properties of rice husk ash using FESEM

3.14.2 Characterization of products from different stage

The following samples were collected from different stages of the experiments:

- Sodium silicate solution from filtration of alkaline extraction stage as filtrate
- Residue (containing unreacted silica, un-burnt carbon and water insoluble impurities) from filtration stage as filter cake
- Precipitated silica from acid precipitation stage

The collected above products from different stages of experiments were characterized and analyzed for investigating the following properties:

The following properties of sodium silicate are investigated by analytical methods:

- Solid content
- Alkali content
- Silica content
- Specific gravity

The above properties are characterized using various characterizations Instruments:

- Specific gravity by Hydrometer
- Silica and alkali content by XRF
- Morphological characteristics by FESEM

The following properties of precipitated silica are characterized using various characterization methods:

- Purity of silica by hydrofluoric acid method
- pH by pH meter
- Tap density by measuring cylinder
- Presence of chloride and sulphate by silver nitrate and barium chloride respectively
- The structure of precipitated silica by XRD
- Chemical composition by XRF
- Morphological characteristics by FESEM

3.14.3 Characterization techniques

The following instrumental techniques were employed to characterize the research materials and products obtained from different stages of experiments.

- X-ray fluorescence (XRF) for chemical composition analysis
- X-ray diffraction (XRD) for phase analysis
- Field Emission Scanning Electron Microscope (FESEM) for morphological analysis

Determination of chemical composition of rice husk ash and precipitated silica by X-ray fluorescence (XRF) technique

X-ray fluorescence (XRF) was used to analyze the following characteristics:

- Chemical composition of rice husk ash
- Chemical composition and the ratio of silica/sodium oxide of sodium silicate
- Purity of precipitated silica

X-ray fluorescence (XRF) was conducted to obtain the composition of oxides in rice husk ash. It is a powerful quantitative and qualitative analytical tool for elemental analysis of materials. It is ideally suited to determination of composition and elemental concentration by weight of solids. Two general types of XRF are wavelength dispersive X-ray fluorescence (WDXRF) and energy dispersive X-ray fluorescence (EDXRF). In this study, WDXRF was used to investigate the oxide composition of rice husk ash.

XRF technology provides one of the simplest, most accurate and most economic analytical methods for the determination of the chemical composition of many types of materials, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology. It is non-destructive and reliable, requires no, or very little, sample preparation and is suitable for solid, liquid and powdered samples [58]. It can be used for wide range of elements and provide detection limits at the sub-ppm level; it can also measure concentrations of up to 100% easily and simultaneously [59].

Theory of X-ray fluorescence

When the elements in a sample are excited with high-energy, short wavelength radiation (e.g., X-rays), they can become ionized. If the energy of the radiation is sufficient to dislodge a tightly-held inner electron, the atom becomes unstable and an outer electron replaces the missing inner electron. When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. The emitted radiation is of lower energy than the primary incident X-rays and is termed fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the sample [60]. The basic concept for all XRF spectrometers is a source, a sample, and a detection system (Fig. 3.14). In most cases for XRF, the source is an X-ray tube. The elements in the sample are excited and characteristic radiation emitted from them diffract into different directions through an analyzing crystal or monochromator. While the sample position is fixed, the angles of the crystal and detector are changed in compliance with Bragg's law so that a particular

wavelength can be measured. A detector measures the fluorescence radiation emitted from the sample.

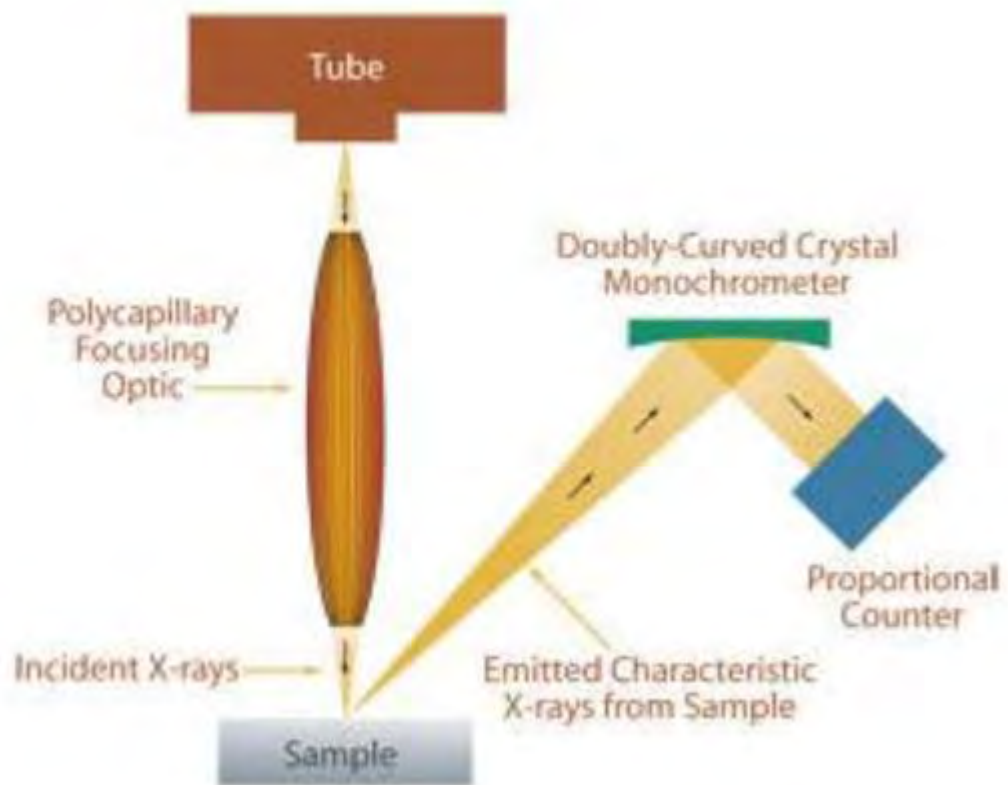
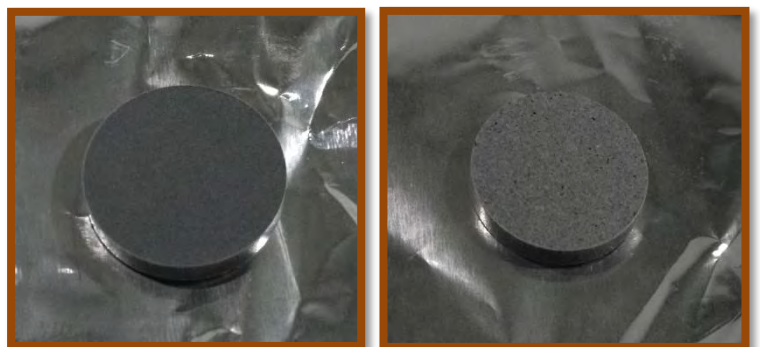


Fig. 3.14 Schematic diagram of X-ray fluorescence.



(a)



(b)

Fig. 3.15 (a) XRF machine used in this research; (b) Tablet preparation for XRF test.

Determination of silica structure and presence of contaminants in rice husk ash through X-Ray Diffraction (XRD) analysis

X-ray diffraction (XRD) is used to analyze the following characteristics:

- Determination of crystal structure of silica in rice husk ash
- Presence of crystalline impurities in rice husk ash
- Crystal structure of precipitated silica

Principle

X-ray diffraction (XRD) is a nondestructive analytical technique mainly used for the phase identification and structural characterization of crystalline materials.



Fig. 3.16 X-Ray Diffraction (XRD) machine.

X-rays are a type of electromagnetic radiation. The wavelength of X-rays is approximately 1 Å which has the same size equivalent to that of an atom. To detect the diffracted X-rays, an electronic detector is placed on the other side of the sample from the X-ray tube and rotated through different Bragg's angles. The goniometer keeps track of the angle (θ), and the detector records the detected X-rays in units of counts/sec and sends this information to the computer.

In order to identify the unknown substance, the powder diffraction pattern is recorded with the help of a camera or a diffractometer and a list of d-values and the relative intensities of the diffraction lines is prepared. These data are compared with the standard line patterns available for various compounds in the Powder Diffraction File (PDF) database. It contains line pattern of more than 60,000 different crystallographic phases. In practice, for any unknown sample, the appearance of three most intense characteristic lines from the standard PDF line pattern is a sufficiently convincing evidence of the existence of a crystalline phase in either a homogeneous substance or even in a multi component mixture. It may be relevant to mention here that while the peak positions and intensities associated with an X-ray diffraction pattern enable qualitative analysis, these parameters are also useful for lattice constant determination and stress determination of the sample.

Distinct peaks in the result indicate the presence of crystalline substance in the sample. Sometimes extra peaks might appear due to the impurity or structural transformation after thermal treatment. In fact, the intensity, width and position of peaks in the patterns reflect information about structure, quantity, texture etc. of crystallites. The amorphous structure is indicated by a background hump at peak position of approximately 22° on the diffractogram.

Table 3.5: Diffraction peaks of crystalline silica [61]

Type of silica crystal	2θ scale		
	Primary	Secondary	Tertiary
Quartz	26.66	20.85	50.16
Cristobalite	21.93	36.11	31.46
Tridymite	21.62	20.50	23.28
Amorphous	Background hump at 22°		

Topography and morphological studies of rice husk ash and precipitated silica using Field Emission Scanning Electron Microscope (FESEM)

FESEM is used to observe the morphology of following products:

- Rice husk ash collected from various rice mills
- Precipitated silica

A FESEM is microscope that works with electrons (particles with a negative charge) instead of light. These electrons are liberated by a field emission source. The object is scanned by electrons according to a zig-zag pattern. A FESEM is used to visualize very small topographic details on the surface or entire or fractioned objects. Researchers in biology, chemistry and physics apply this technique to observe structures that may be as small as 1 nanometer (= billion of a millimeter).

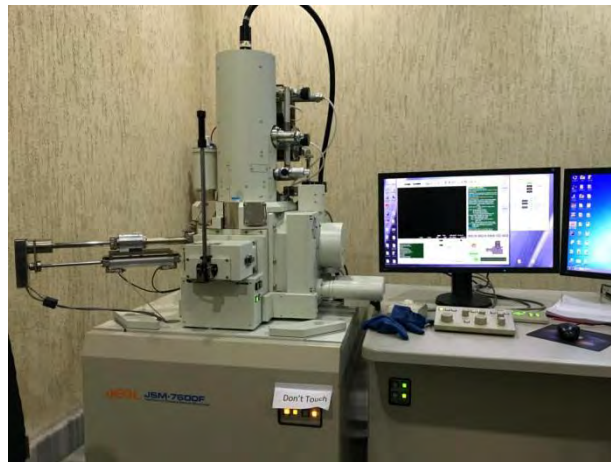


Fig.3.17 Field Emission Scanning Electron Microscope (FESEM).

Electrons are liberated from a field emission source and accelerated in a high electrical field gradient. Within the high vacuum column these so-called primary electrons are focused and deflected by electronic lenses to produce a narrow scan beam that bombards the object. As a result, secondary electrons are emitted from each spot on the object. The angle and velocity of these secondary electrons relates to the surface structure of the object. A detector catches the secondary electrons and produces an electronic signal. This signal is amplified and transformed to a video scan-image that can be seen on a monitor or to a digital image that can be saved and processed further.

Procedure: The FESEM-(JEOL JSM 7600F) field emission scanning electron microscope was used to characterize the morphologies of the samples (Fig. 3.17). Powder samples were adhered with carbon tape that was attached to a Copper stub. Then sample holder was mounted on a holder and inserted in FESEM. The micrographs obtained from FESEM analysis was used for microstructural study. Selected areas of interest were focused and micrographs were taken.

CHAPTER FOUR
RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

In this chapter the results of the experimental works will be presented and discussed. The discussion will be segmented into five parts namely, (i) characterization of as-received rice husk ash (ii) purification of as-received rice husk ash (iii) quantitative results of the experiments conduct in this research (iv) characterization of products obtained from different stages of experiments (v) Influence of different reaction variables to prepare high purity precipitated silica (vi) characterization of as-produced precipitated silica.

4.1 Characterization of As-received Rice Husk Ash (RHA)

Rice husk ash was pre-treated by acid-leaching method to reduce the metal impurities level. The rice husk ash collected from local rice mills was characterized by X-Ray Fluorescence (XRF) to determine the chemical composition and X-Ray Diffraction (XRD) to know the crystal phases present in the ash.

4.1.1 Optical image of rice husk ash (as-received)

Photographs of the rice husk ash samples obtained from the different zones are shown in Fig. 4.1. The rice husk ash had a charcoaled black and greyish appearance with some brown color and a gritty feel in between fingers.



Fig. 4.1 Optical images of rice husk ash.

From the Fig. 4.1, it is observed that the ashes are mostly black with gray particles with visual impurities like sand, un-brunt rice husk, and un-burnt carbon which were generated as result of incomplete combustion during the rice husk burning in boiler. The burning of rice husk in presence of air always leads to the formation of silica ash, which varies from the gray to black depending on inorganic impurities and unburned carbon. According to literature, rice husk ash can be divided into following categories including high-carbon char, low-carbon gray ash, and carbon-free white ash [10,62].

4.1.2 Chemical composition analysis of rice husk ash

High silica content and low levels of elemental impurities are necessary pre-requisites for synthesis of high purity precipitated silica from rice husk ash [63]. Accordingly, chemical composition analysis of as received rice husk ash was performed by X-Ray fluorescence spectroscopy (XRF). The main oxide present in the as-received rice husk ash value are summarized and compared to literatures values are tabulated below in Table 4.1

Table 4.1: Chemical composition analysis of rice husk ash by XRF

No. of Sample	Chemical Composition, Wt%										
	1	2	3	4	5	6	7	8	9	10	11
	SiO ₂	Al ₂ O ₃	K ₂ O	MgO	Fe ₂ O ₃	MnO	SO ₃	ZnO	P ₂ O ₅	CaO	Na ₂ O
Sample-1	90.83	1.42	1.06	0.57	0.42	0.24	0.47	0.01	2.25	-	-
Sample-2	96.38	1.11	-	0.75	0.67	0.19	0	0.02	-	-	-
Sample-3	90.17	0.59	2.35	0.31	0.42	0.24	0.47	0.01	2.67	-	-
Sample-4	91.87	0.17	1.03	1.25	0.54	0.34	0.16	0.02	2.36	1.08	1.27
Sample-5	88.38	1.07	0.89	1.12	0.68	-	2.03	0.02	1.15	1.02	2.95
Sample-6	90.82	0.54	1.89	1.33	0.69	0.24	1.67	0.01	2.31	-	-
Sample-7	92.79	0.42	2.05	0.64	0.52	0.07	0.2	0.01	1.16	1.89	0.2
Sample-8	97.24	0.66	-	0.63	0.38	0.2	-	0.01	-	-	-
RHA [64]	86.9-97.3	n/a	0.58-2.5	0.12-1.96	0.54	n/a	n/a	n/a	0.2-2.85	n/a	0.0-1.75

According to XRF analysis, rice husk ash contains 88% - 97% SiO₂ and the rest contains following elements (in oxide form) in traceable amount: 0.17-1.42% Al₂O₃, 0.89-2.35% K₂O, 0.31-1.33% MgO, 0.38-0.69% Fe₂O₃, 0.07-0.34 MnO, 0.16-2.03% SO₃, 0.01-0.02 ZnO, 1.15-2.67% P₂O₅, 1.02-1.89% CaO and 0.2-2.95% Na₂O.

It is observed that the collected rice husk ash has mostly silica of 90 - 97 wt%, which is well within the range of silica content of rice husk ash in literature publications. The “n/a” in the last column of Table 4.1 indicates that no corresponding data was found from the reference source. The silica amount in the as-received rice husk ash is however quite pure enough and among the samples, sample 6, 7 and 8 were selected for the intended purpose of this research work.

It is also evidenced that, the ash produced from the rice husk burning contains small amounts of other composition considered as impurities. The most common trace of chemical composition in rice husk ash are the oxides of aluminium, potassium, magnesium, iron, manganese, sulfur, zinc, phosphorous, calcium and sodium. Differences in composition may occur due to geographical factors, type of ground, year of harvest, types of boiler used in Rice production, etc. [54]. Another possibility can be due to adherent soil particles on the rice husks since no pre-cleaning treatment was done before combustion [54].

4.1.3 Reactive amorphous silica content and moisture content of rice husk ash

The reactive amorphous silica was determined by alkaline extraction method and moisture content was checked by hot air oven drying method.

The range of percentage of reactive amorphous silica was 67% to 92%. The moisture content of rice husk ash was varied from 0.1% to 6%. Differences in percentage of reactive amorphous silica may occur due to the control parameters of boiler in rice mills. Most of the water glass solutions prepared from tested rice husk ash was looked like brownish to greyish color due to presence of un-burnt rice husk in ash as impurities.

Table 4.2: Chemical analysis of rice husk ash

Sample no.	Source	Type of boiler used in rice mill	Reactive amorphous silica content (%)	Moisture content
Sample - 1	Comilla zone	Chain-grate	76%	4%
Sample -2	Sherpur zone	Reciprocating	88%	0.5%
Sample - 3	Ashugonj zone	Chain-grate	74%	4%
Sample - 4	Brahmanbaria	Chain-grate	77%	3%
Sample -5	Comilla	Chain-grate	67%	5%
Sample - 6	Bogra	Reciprocating	76%	6%
Sample - 7	Mymensingh	FBC	85%	0.1%
Sample - 8	Nator	FBC	92%	1%

This difference in the amount of the extracted silica suggested the fact that the regional variation had obvious effect on the silica content of the rice husk ash and should be taken into consideration before using rice husk ash for the production of water glass adhesive on the commercial production.

4.1.4 Phase analysis of rice husk ash

The X rays diffractograms of the rice husk ash are presented in Fig. 4.2. The rice husk ash diffractogram indicates the presence of silica in the crystalline form due to the presence of cristobalite ($2\theta = 21.9$) and the amorphous structure is indicated by background hump on the diffractogram. The crystalline, amorphous silica, or presence of both depends directly on the temperature of burning or the method of ash attainment. When the burning temperature of the rice husk is high, the silica contained in the ash is predominantly crystalline. Crystalline silica had quantified when burning temperature was around of 1000°C. It was found that rice husk ash with predominant crystalline silica, getting 83% of crystalline silica, at temperature of 1350°C; while in the range of temperature 450-700°C, the silica was found mostly in amorphous phase [65].

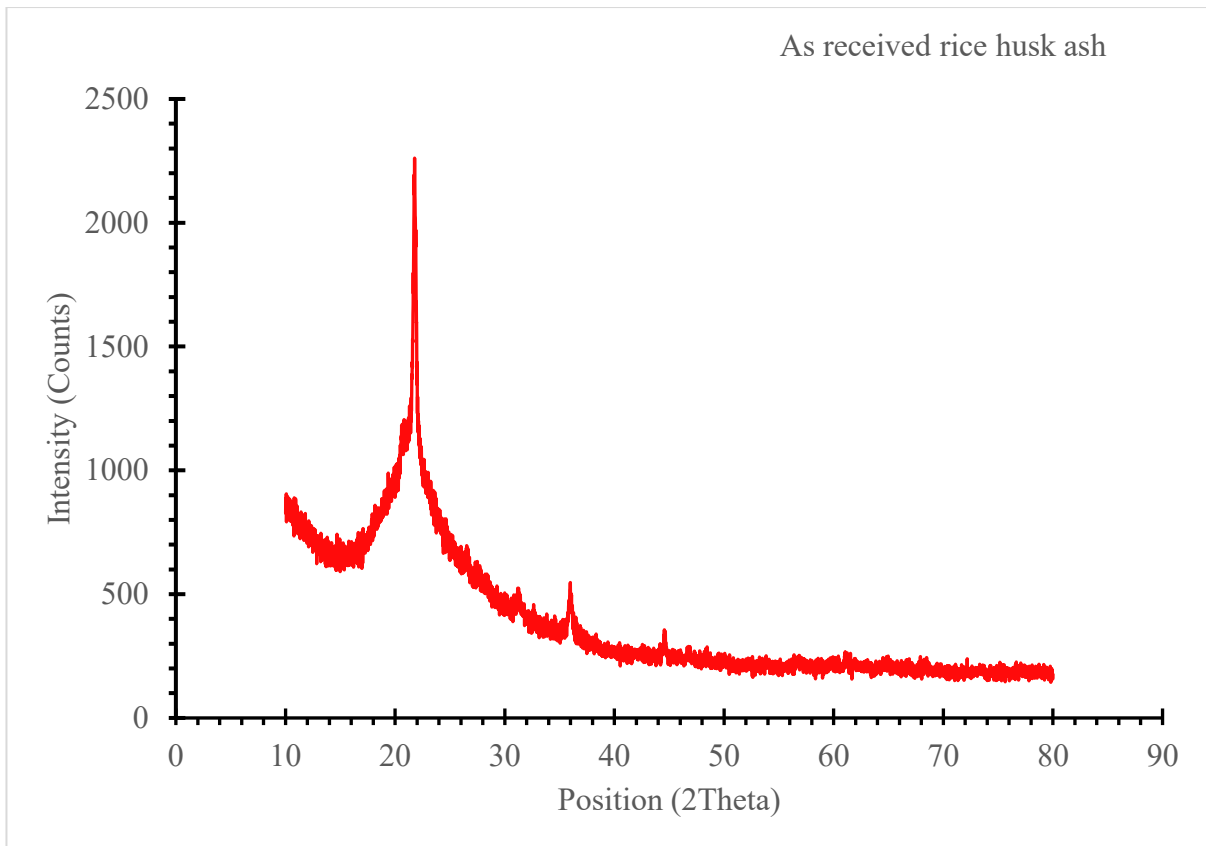


Fig. 4.2 XRD result of as-received rice husk ash.

The structure of silica may determine its reactivity and degree of health danger. Crystalline silica is less reactive and deemed carcinogenic, whilst the amorphous silica is rather reactive and with no harmful effect [10,66].

4.1.5 Morphological properties of rice husk ash

The morphological features of the as-received rice husk ash observed by scanning electron microscope (SEM) is shown in Fig. 4.3. The micrograph was taken under the secondary electron imaging mode (SEI) at a magnification of 10000X and 30000X. As can be seen from Fig. 4.3 that the as-received rice husk ash shows a porous and multifaceted particle shape and size. The main components of rice husk include hydrated silica, cellulose and hemi cellulose component totaling a 55-60% and lignin component of approximately 22% [66,67]. The porous and honeycomb morphology seen in Fig. 4.3 can be attributed to the burning out of the organic component in the rice husk during combustion. The hydrated silica subsequently polymerizes to form a skeletal silica network which may explain the flaky and honey comb-like structure in the SEM micrograph.

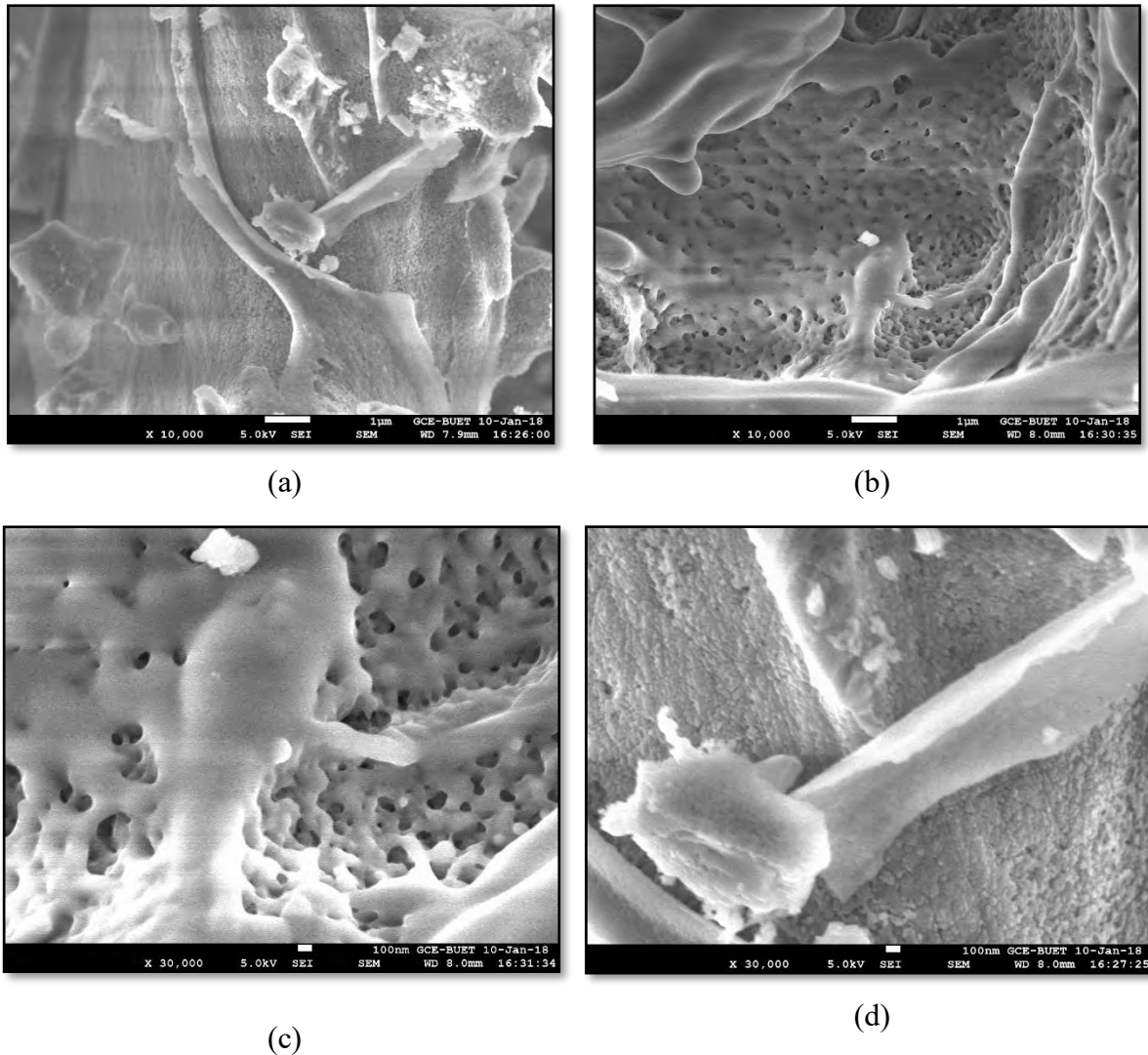


Fig. 4.3 SEM micrograph of rice husk ash (as-received) (a) SEM image of rice husk ash (1 μm; x 10,000); (b) SEM image of rice husk ash (1 μm; x 10,000); (c) SEM image of rice husk ash (100 nm; x 30,000); (d) SEM image of rice husk ash (100 nm; x 30,000).

4.2 Purification of As-received Rice Husk Ash (RHA)

The quality and purity of precipitated silica are depending on acid leaching process of rice husk ash. Metal impurities from rice husk ash hamper the purity level of precipitated silica. Metal impurities cannot be removed by filtration. So, to get iron free silica, acid leaching process is required. The temperature in acid leaching process is very important factor to remove metal impurities from rice husk ash [68].

Three nos of experiments (Table 4.3) were conducted to find out the optimum temperature and time of acid leaching and optimum concentration of hydrochloric acid.

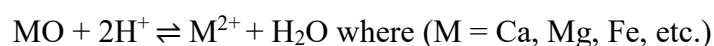
Table 4.3: The results of the acid leaching of rice husk ash

SL No.	Parameters	Exp-1			Exp-2			Exp-3		
1.	Rice husk ash, kg	1			1			1		
2.	Molarity of hydrochloric acid	1M			2M			3M		
3.	Leaching temperature (°C)	60	80	90	60	80	90	60	80	90
4.	Silica content of rice husk ash	98.34	98.45	98.65	99.6	99.64	99.75	97.5	98.8	97.95
5.	Reaction time, hour	2	2	2	2	2	2	2	2	2
6.	Removal of impurities, %	85	85.5	85.84	94.75	95	95.2	89.5	90.25	90

4.2.1 Effect of leaching treatment

In order to access the efficacy of the leaching step and to determine the best leaching condition, the concentration (ppm) of impurities in the leached sample is ratioed to the concentration of impurities in as-received rice husk ash. It was observed that the acid leaching leads to higher SiO₂ contents in the ash. It also decrease the amount of alkali contaminates such as K₂O and Na₂O. Past research [69,74] suggested that a higher surface area was attainable with the silica particles obtained through HCl acid leaching process of rice husk ash. This may be ascribed to the cross-linking network of the porous silica particulate which made particle size determination very hard due to the irregular shape of the particles.

Acid leaching uses the advantage of silica being relatively insoluble in acidic media [69,70]. Direct acid leaching uses the chemical mechanism of proton attack to achieve metal oxides removal from rice husk ash. The H⁺ ion displaces the cation from the ash particle matrix to induce dissolution of the metals. The H⁺ ions react with the solid aluminium, iron and other metal compounds that are progressively exposed on the surface and within the pores of the ash particles as the leaching proceeds [71]. The chemical reactions describing the dissolving of the major element compounds are represented as follow:



It is obvious from the above reaction that the leaching process is a solid liquid two phase reaction involving different species. It also suggested that a substantial amount of HCl added would be consumed to dissolve other unwanted metal species [72,73]. Because of this reason, the concentration of HCl might have to achieve an acceptable leaching rate of rice husk ash.

The leaching results of rice husk ash are shown in Fig. 4.4. As expected, faster leaching rate and maximum silica percentage was obtained using high concentration of HCl. However, using a highly concentrated acid not only poses corrosion problems to equipment, but also increases the operation cost. In terms of leaching kinetics and operational conditions, an optimum HCl concentration should be the concentration at which the percentage of removal of impurities present in rice husk ash and reaction rate was maximum [70].

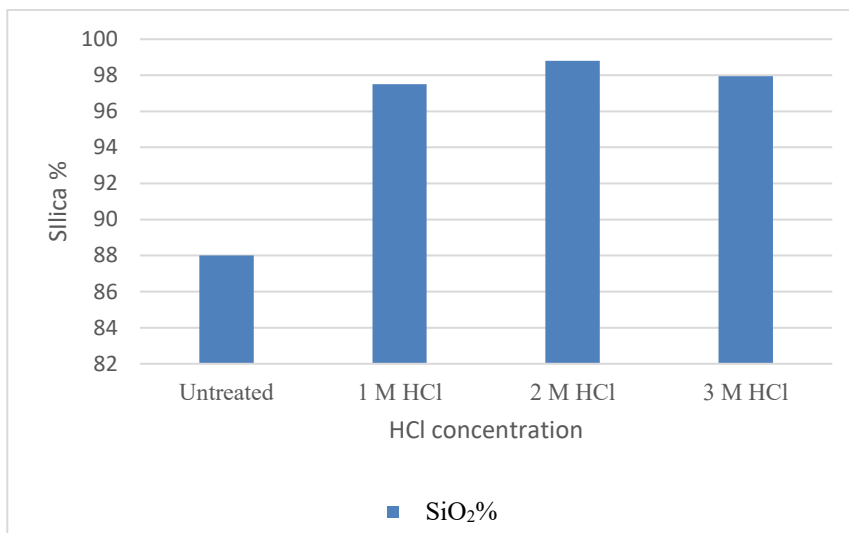


Fig. 4.4 Effect of HCl concentration on SiO₂%.

Fig. 4.4 shows the leaching test results for HCl treatment (1-3 M) for two hours duration. It seems that silica content in rice husk ash is increased from 88 % to about 99% for 2M HCl concentration.

To identify the suitable leaching model and mechanisms of removal of impurities from rice husk ash with hydrochloric acid solution, the leaching kinetic experiments were conducted at different temperatures with 1M and 2M hydrochloric acid solution.

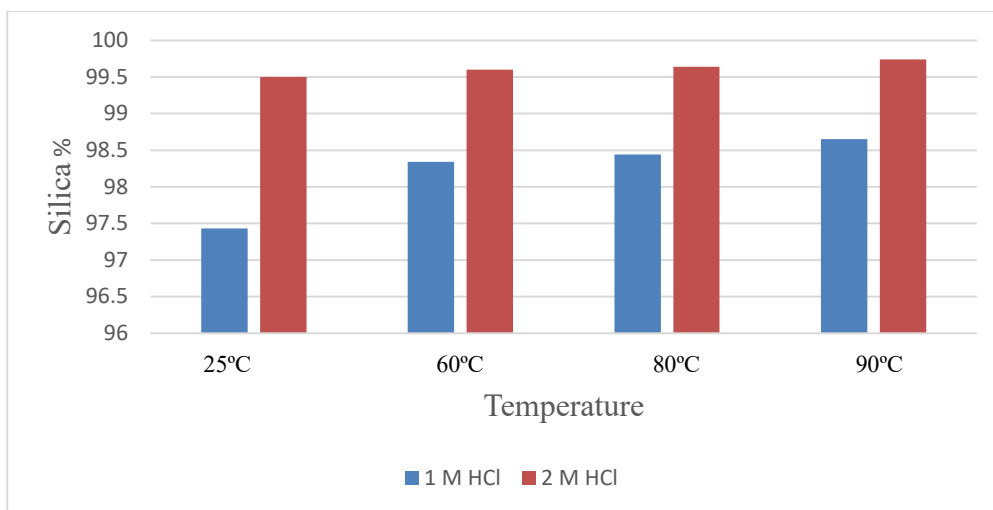


Fig. 4.5 Effect of acid leaching temperature on SiO₂%.

Fig. 4.5 shows that temperature effect is insignificant for 2M HCl concentration, whereas for low concentration (1M HCl), it has more substantial impact and become more effective with increasing temperature as expected.

Leaching reaction is generally endothermic. Increasing the leaching temperature would therefore enhance the leaching reactions. At higher temperature, leaching chemical species could have higher diffusion rates, due to the increased thermal or activation energies [74]. Both scenarios are expected to enhance the leaching process.

The analysis of the impurities and the effect of the chemical treatment on rice husk ash are given in Fig. 4.6. It indicates that, inorganic impurities present in rice husk ash are effectively removed by leaching with HCl. A similar observation was made by Hunt et al. [75] in their study on leached rice husk ash.

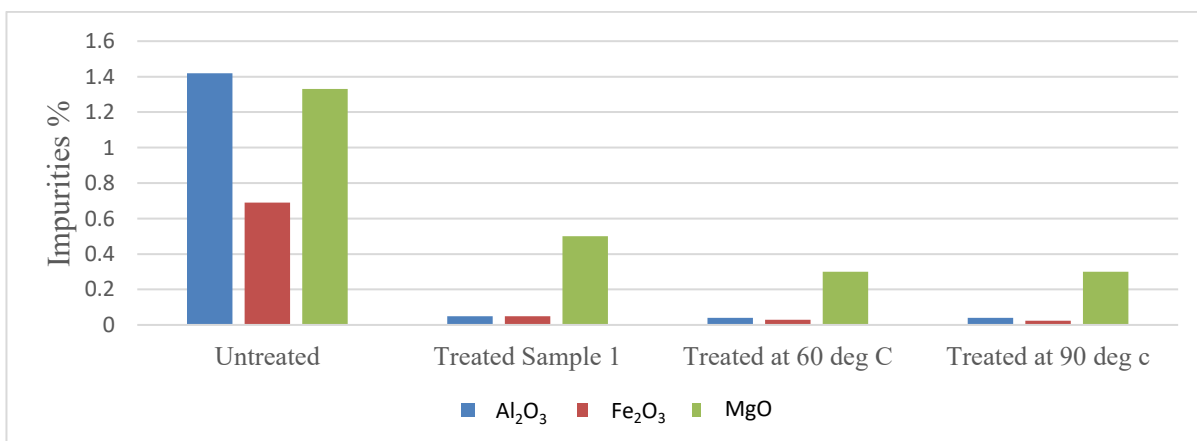


Fig. 4.6 Presence of oxide content in treated and untreated rice husk ash.

4.3 Quantitative Results of the Experiments Conducted in this Research

After the leaching by acid solution, slurry of ash was prepared with Sodium hydroxide solution having specific molarity (0.75-1.50) and heated the solution under desired temperature (130-150°C) and pressure (0 – 2.5 bar) for specific period (1-6 h). A clear diluted sodium silicate solution was obtained after filtering the slurry.

Table 4.4 shows the result for the various analysis carried out on the produced sodium silicate by alkali extraction of rice husk ash.

Table 4.4: Various analysis parameters used to produce sodium silicate from rice husk ash

Sl. No.	Parameters	Quantity				
		Experiment-1	Experiment-2	Experiment-3	Experiment-4	Experiment-5
1.	Ratio of RHA and caustic soda	1.96	2.22	2.44	2.70	2.94
2.	Rice husk ash, kg	1	1	1	1	1
3.	Total Silica in rice husk ash, kg	0.80	0.80	0.80	0.80	0.80
4.	Caustic soda flakes, kg	0.51	0.45	0.41	0.37	0.34
5.	Sulphuric acid, L	0.43	0.42	0.40	0.36	0.33
6.	Water to rice husk ash ratio	7:1	7:1	7:1	7:1	7:1
7.	Temperature, °C	150	150	150	150	150
8.	Reaction time (h)	3	3	3	3	3
9.	Final ratio of silica and sodium oxide in silicate solution	1.88	2.11	2.27	2.29	2.31
10.	Dry silica, kg	0.66	0.65	0.63	0.56	0.52
11.	Efficiency of silica extraction, %	82.77	80.96	78.30	70.52	64.60

From Table 4.4, it was found that, optimum ratio of rice husk ash/caustic soda was 2.44 (experiment -3) for the production of commercial precipitated silica.

These experiments (Experiment no. 1-5) had been conducted in a pressure vessel at temperatures of 130 -150°C, with 3-4 hours of reaction period, and the behaviors for the silica extraction were observed. 1 kg of rice husk ash was mixed with 7 L of water having different concentration (0.51 kg, 0.45 kg, 0.41 kg, 0.37 kg and 0.34 kg) of sodium hydroxide keeping all other parameters constant. Experiments were carried out to study the effect of the ratio of rice husk ash/NaOH and the molarity of NaOH solution on yield of silica.

The diluted sodium silicate solution, after alkali extraction of rice husk ash, was acidified by sulphuric acid to reduce pH of the solution to ~7. At around pH 7, precipitation process of silica was completed. The precipitated silica was then washed by hot water to remove sodium sulfate produced from the precipitation stage. The washed silica was aged, dried and pulverized to get fine powder precipitated silica.

Final product, precipitated silica, was characterized by XRF for its chemical analysis and purity, by XRD for identifying crystal phase structure of silica, and FESEM for topography and morphology. The characterization results are shown and discussed elaborately in section 4.6. This process was able to meet the international requirement with respect to the quality of silica. XRF results showed that purity of precipitated silica was 97% - 98%. XRD result of the precipitated silica showed a broad peak zone centered near $2\theta = 22.2^\circ$ signifying the amorphous nature of silica [76]. The silica obtained by alkaline extraction at low temperature was completely amorphous. This was due to the fact that sodium hydroxide solubilizes only amorphous silica, which is subsequently precipitated.

Table 4.5 shows quantitative analysis of the experiment (Exp. no.1-3).

Table 4.5: Results for the various analysis of produce precipitated silica from sodium silicate

Sl. No.	Parameters	Result of Experiment		
		Exp-1	Exp-2	Exp-3
Output of the experiment				
1	Precipitated silica solution after acidification, gm	200	190	195
2	Gelation time, minutes	60	120	30
3	Precipitated silica gel after vacuum filtration, gm	150	155	146
4	Precipitated silica gel after purification, gm	150	154	146
5	Final product after aging and drying, gm	65	70	70
Yield of Precipitated Silica				
1	Dry silica, gm	65	70	70

It is observed from Table 4.5 that the quantity level of precipitated silica solution after acidification are typically slightly varied in different experiments. This is may be due to increased reactant materials as result of increased amount of charging materials or may be due to sodium silicate concentration. Gelation time depends on silica concentration present on sodium silicate solution. Lower silica concentration results longer period of gelation time [77].

4.4 Characterization of Products Obtained from Different Stages of Experiments

Table 4.6 shows the characterization of products obtained from different stages of experiments by analytical methods (Exp. No. 1-3). The data in the Table 4.7 is made clearer when the extractable amorphous silica in rice husk ash found maximum with increasing silica content in rice husk ash. The optimum silica yield occurs at charge composition having 1.2 g/ml – 1.25 g/ml of sodium silicate solution and 1.1 g/ml H₂SO₄, when acidification was carried out in optimum temperature and atmospheric pressure. The traces of chloride and sulphate is minimum (0- 0.05) and silica content found maximum 99.8% after drying, aging and grinding.

Table 4.6: Characterization of products obtained from different stages of experiments

Sl. No.	Parameters	Result of Experiment		
		Exp-1	Exp-2	Exp-3
Raw material characterization				
1	Silica content in rice husk ash by XRF, %	92.79	90.28	97.24
2	Extractable amorphous silica in rice husk ash by analytical method, %	80	78	82
3	Molarity of NaOH	8.33	8.33	8.33
4	pH of Na-silicate solution	12-13	12-13	12-13
5	Specific gravity of Na-silicate solution	1.20 g/ml	1.25 g/ml	1.22 g/ml
6	Concentration of H ₂ SO ₄ solution	1.1 g/ml	1.1 g/ml	1.1 g/ml
Product characterization after Acidification				
1	pH of gel solution	6.8	6.7	6.7
2	Trace of chloride (as NaCl), %	0.08	0.05	0.02
3	Trace of sulphate (as Na ₂ SO ₄), %	0.02	0.05	Nil
4	Silica content, %	98.87	99	99
Product characterization after filtration and purification				
1	pH of gel	6.5	6.5	6.5
2	Trace of chloride (as NaCl), %	0.026	Nil	-
3	Trace of sulphate (as Na ₂ SO ₄), %	Nil	Nil	-
Product characterization after drying, aging and grinding.				
1	Appearance	White Crystal	White Powder	White powder
2	Silica content, % (chemical analysis method)	99	99	99.8
3	Bulk density	0.60 g/cc	0.40 g/cc	0.1 g/ml
4	Loss on Ignition, % by mass	3.0	2.7	3
5	Moisture, % by mass	3	2.7	3
6	pH (5% aqueous slurry)	6.5	6.5	6.5
7	Iron Content, ppm	Nil	Nil	Nil
8	Soluble salts (sulphates and Chlorides), % by mass	0.02	0.05	Nil
9	Heavy metals (as Pb), ppm	Nil	Nil	Nil
10	Particle size (micron)	0.5 – 4.75	2.5 -17.5	2.5 – 14

4.5 Influence of Different Reaction Variables to Prepare High Purity Precipitated Silica

Silica particles carry negative charges in alkaline, neutral or weakly acidic solutions, which retard the association by electrostatic repulsion, particles repel each other at a pH above 11 [78]. As the pH is reduced or through charge screening and reducing the dielectric constant of the aqueous phase, silicate species aggregate to form higher-order oligomers. The silanol groups within the polymers condense to build larger particles. Polymer chains and eventually gel is formed by the aggregation of these particles. Gelation occurs when particle aggregation ultimately forms a uniform, three-dimensional network of silicate particles. When gelation begins, the initially transparent solution of Na-silicate starts to become cloudier. That cloudiness thickens as the gel develops, and the gel's appearance is sometimes used as a qualitative measure of gelation time.

The polymerization rate of Na-silicate is affected by the pH, silicate concentration, temperature and concentration of the divalent cations [79,80]. The influencing parameters and their effect on silicate polymerization are discussed in below subsection.

4.5.1 Effect of pH and silicate content

The pH of different sodium silicate solutions was obtained by diluting the initial sodium silicate with distilled water. A considerable difference in the pH is observed for diluted sodium silicate below 3 wt% (Fig. 4.7). A sodium silicate content ranging between 1.2 wt% and 2 wt% is deemed as practical for the purpose of this work.

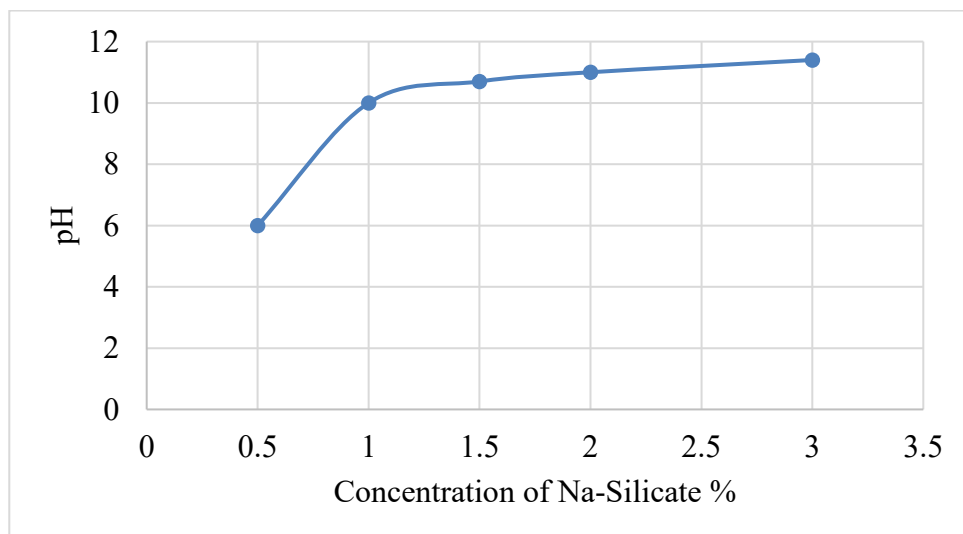


Fig. 4.7 Effect of pH on different Na-silicate contents from 0.5 wt% to 3 wt% by diluting with distilled water.

The added H₂SO₄ to solutions with Na-silicate contents (2 wt%) is plotted with the corresponding pH in Fig. 4.8.

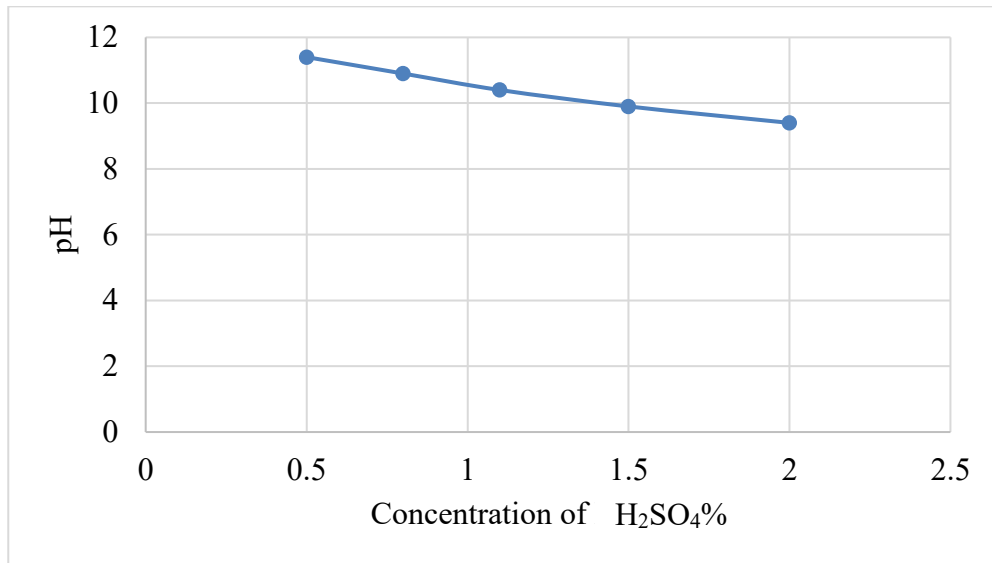
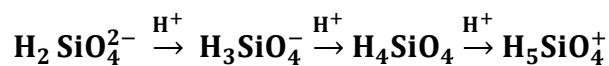


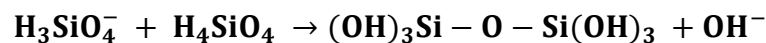
Fig. 4.8 Corresponding pH as a function of H₂SO₄ concentration.

All Na-silicate contents show similar trends, i.e., pH decreases linearly up to a certain point, after which the rate of pH reduction increases with the added acid. The gradients of pH as a function of the increased H₂SO₄ concentration depend on the Na-silicate content, i.e., the higher the Na-silicate wt%, the lower the gradient owing to the increase in buffer capacity.

An-Peng [79] suggested the following reactions as the pH is reduced, where silicic is formed:



At high pH, $\mathbf{H_2SiO_4^{2-}}$ and $\mathbf{H_3SiO_4^-}$ are the dominant ions. The dominant species at lower pH (slightly alkaline or neutral) are $\mathbf{H_3SiO_4^-}$ and $\mathbf{H_4SiO_4}$; therefore, the condensation process starts and may be expressed as:



Two silanol groups form a new bond in which an oxygen atom bridges the silicon atoms to produce siloxane [81].

4.5.2 Gelation time

Factors affecting the gelation time are silicate content, pH, concentration of divalent ions (namely Ca^{2+} and Mg^{2+}), temperature and shear rate [82]. This section addresses the influence of various factors in terms of time required for gelation of silica sol and the extent of syneresis of the gel formed shown in Fig. 4.9 – 4.11 below.

Silica sol having SiO_2 content of 1.5% gelled in 40 min at room temperature. When the concentrations of SiO_2 were lower, the period for gelation was longer; whereas at higher concentrations gelation was too rapid for the preparation for laboratory media (Fig. 4.9).

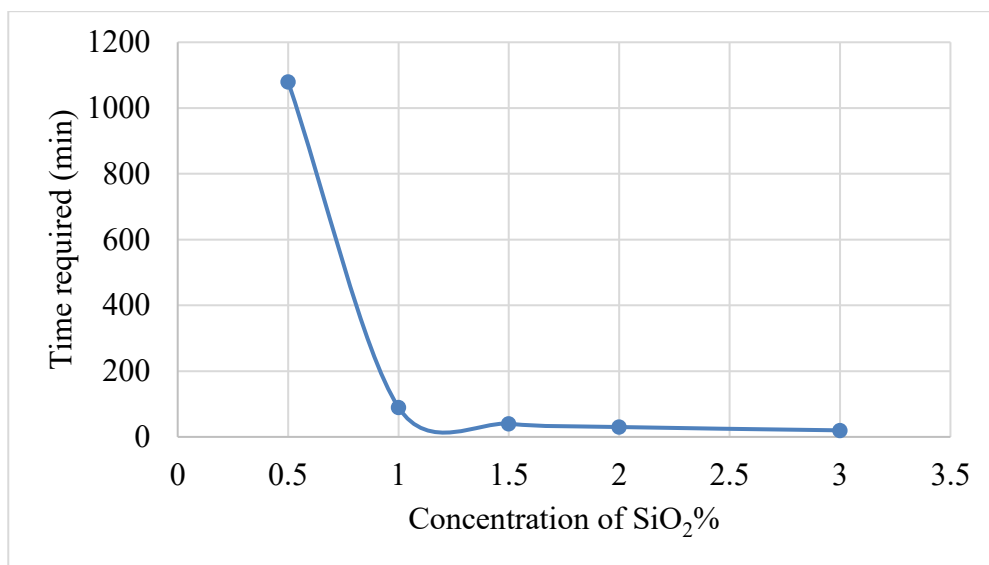


Fig. 4.9 Effect of silica concentration on gelation time.

Gelation time is dependent on the Na-silicate content (Fig. 4.9) and the pH (Fig. 4.10). For a specific pH, the condensation rate of silicic acid increases with silicate content. Lowering the pH for a certain silicate content also increases silicic acid condensation and hence reduces gelation time.

Silica surface area also changed with sodium silicate concentration. This is because of the transformation between nucleation and growth reactions during particle formation [83]. At lower silicate concentrations, gelation occurs much slower. Hence surface area is relatively low. Surface area that increases with silicate concentration is due to the increased number of formed nuclei. For higher silicate concentrations, gelation rate increases. Accelerated growth

of silica on the pore walls leads to a reduction in pore diameter and, hence, reduced sample surface area. This situation indicates that particles growth in the acidified slurry is stable.

If the gelation time is prolonged more than 7 days, gelation does not occur at pH less than 3. At pH 3 solid starts to precipitate, where gel formation is low. Silica yields gradually increases with increasing pH, with a maximum yield occurring at around pH 7. Increasing silica yields, decreasing the gelation time with increasing pH. When the pH is greater than 8, formed gels are unstable and partially redissolved. At pH 11, these gels dissolve almost entirely in water. On the other hand, gelation pH has a great effect on porosity and particle size of produced silica [84].

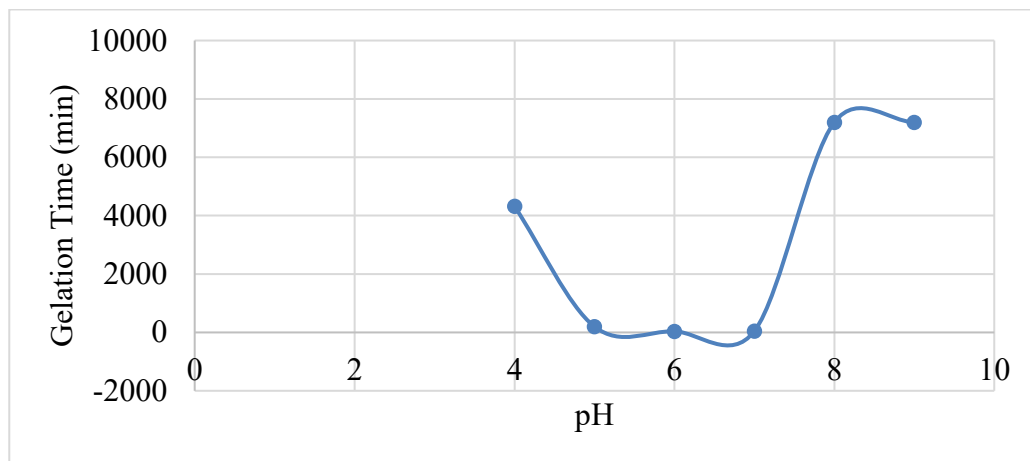


Fig. 4.10 Effect of pH on gelation time.

The effect of temperature on the gelation time is shown in Fig. 4.11. At 1.5 % silica content, while keeping pH 6.0, it seems that, gelation time decreases with increasing temperature. Increasing temperature from 20-50°C increases surface area of silica due to accelerated growth of silica framework with increasing temperature. Also Jurinak and Summers [85] suggested that at fixed pH, the polymerization rate increases as the temperature rises, hence the gelation time decreases.

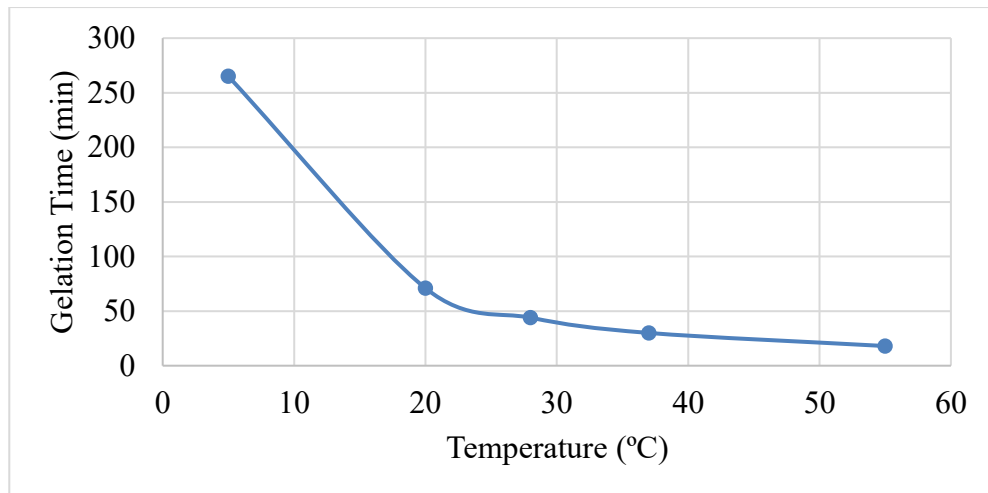


Fig. 4.11 Effect of Temperature on gelation time.

4.5.3 Syneresis

A particulate gel network forms during the precipitation process, when, monomeric silicic acid is formed by mixing aqueous sodium silicate and sulphuric acid, which polymerizes, and eventually, precipitates as solid silica. That gel network is fragmented continuously by a stirrer, resulting in gel fragments. These fragments restructure due to the continuing polymerization. As direct consequence of the restructuring, the gel fragments shrink, and the liquid content is expelled. This process is known as syneresis [86].

The stages from the beginning to increase viscosity, gel network formation reaching a maximum strength. This is then followed by the gel syneresis process, where liquid is expelled from the network to cause gel shrinkage. Typically, there is a period after gelation time, where no shrinkage takes place until the formed gel approaches maximum strength. This has also been reported by Brinker and Scherer [87].

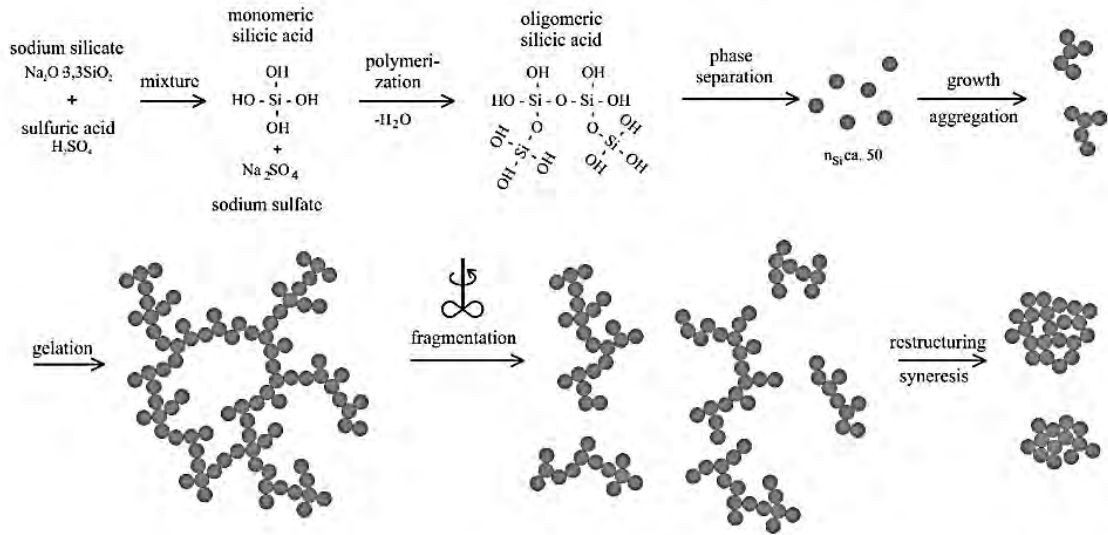


Fig. 4.12 Precipitation process of silica [88].

25°C temperature and pH of 6 is considered as an example to demonstrate the effect of concentration of silica (%) on syneresis (ml). For a given pH, increasing silicate content (wt %) accelerates the starting of shrinkage. Fig. 4.13 shows that, at a given pH, the higher the silicate content, the higher the shrinkage rate and total shrinkage. On the other hand, shrinkage increases with both increasing and decreasing of pH from 6. However, a decreasing trend of shrinkage is observed at pH below 5.

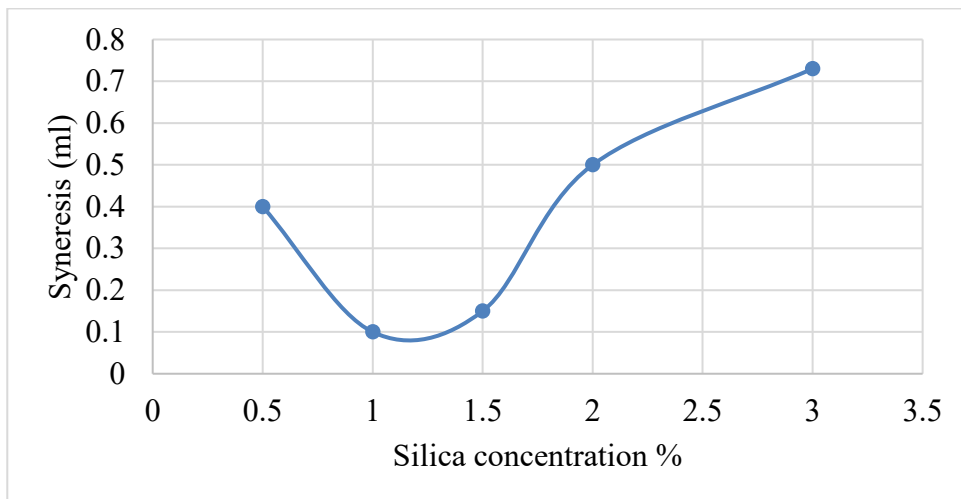


Fig. 4.13 Effect of concentration of silica (%) on syneresis (ml).

pH directly affects the solubility of the monomeric silicic acid. For pH<5, the solubility is constant and very low, but it increases dramatically for pH>5 by several orders of magnitude.

This is due to an equilibrium between the monomeric silicic acid and its deprotonated anion that can be stabilized by water molecules [89]. The equilibrium is shifted to the anion with increasing pH. Thus, pH affects the supersaturation.

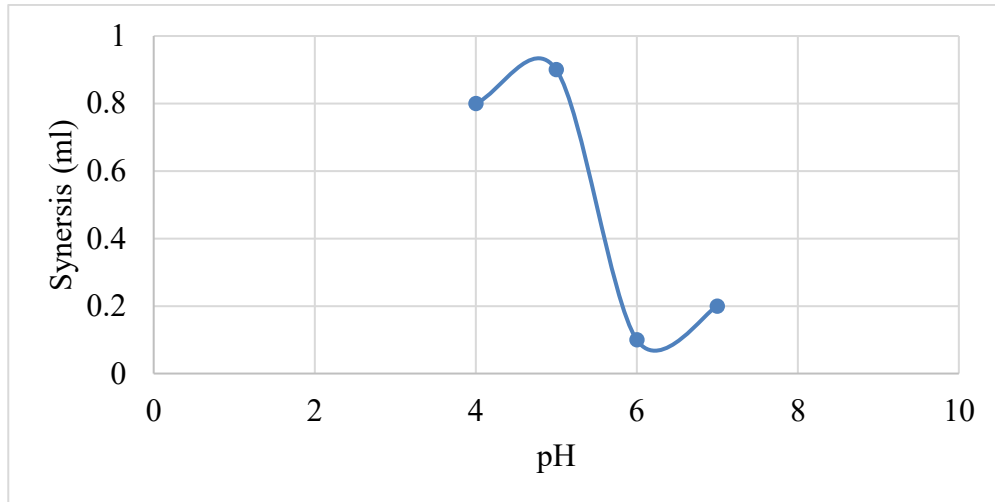


Fig. 4.14 Effect of pH on syneresis (ml) at 1.5 % SiO₂ and temp 25°C

The rate of syneresis usually increases with temperature [90]. Since syneresis involves a kinetic phenomenon, this may be expected. The enclosed pore liquid must move through the solid skeleton to obtain shrinkage. This movement depends on the viscosity of the pore liquid and reaction rate of the polymerization. The latter affects the permeability, and, thus the compliance of the solid skeleton [90]. The viscosity of the pore liquid decreases with increasing temperature, but the reaction rate increases disproportionately. The drainage of the pore liquid becomes the rate-limiting process. It is assumed that the stress produced by the formation of siloxane bonds is lowered by shear deformation rather than volume decrease [86].

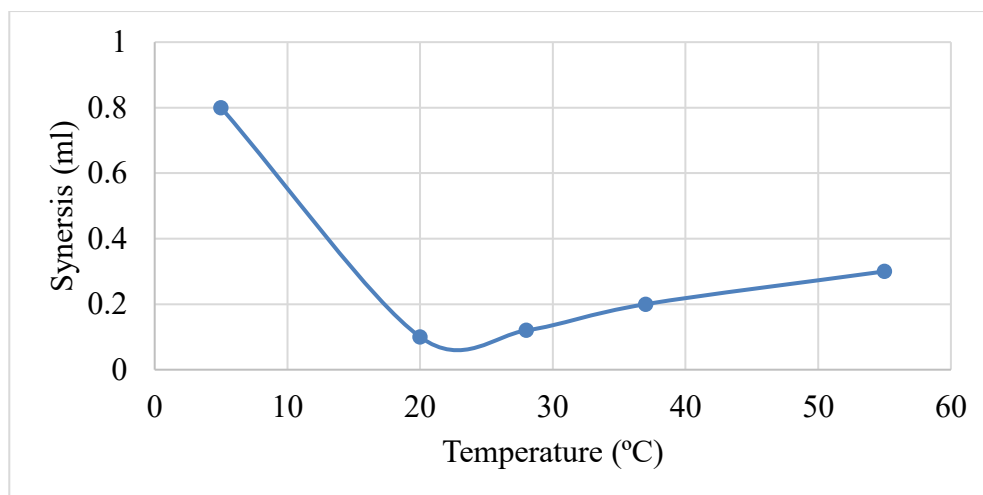


Fig. 4.15 Effect of temperature (°C) on syneresis at 1.5 % SiO₂ and at pH 6

To address the effect of temperature on syneresis, a gel prepared at three different temperatures within 20 – 60°C with a sodium silicate content of 1.5 wt% at a pH of 6.0. As shown in Fig. 4.15, higher temperature accelerates the shrinkage. Syneresis rate at 20, 37 and 55°C are approximately 0.1 ml, 0.2 ml and 0.3 ml respectively.

4.6 Characterization of As-produced Precipitated Silica

A photograph of the as-produced precipitated silica powder after drying and milling is shown in Figure 4.16. The material looked like white free flow powder and slightly greyish.

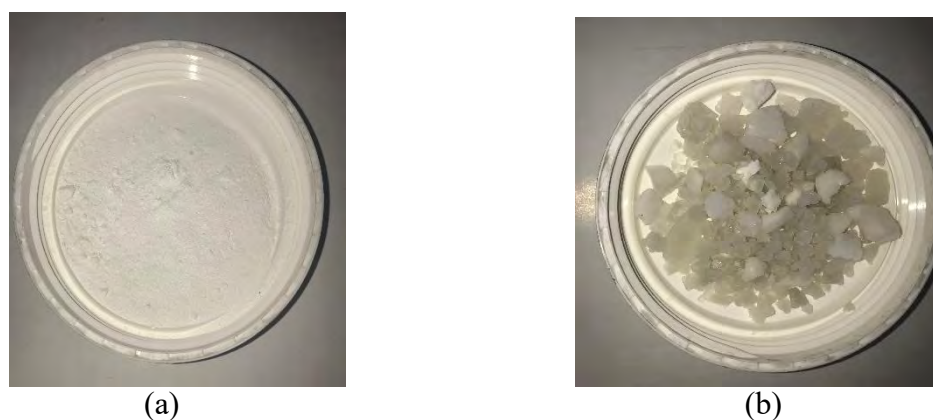


Fig. 4.16 As-produced precipitated silica from rice husk ash (a) White free flow powder; (b) Slightly greyish crystal.

The precipitated silica powder was extracted from obtained ash by NaOH solution. According to the XRD analysis (Fig. 4.17), the extracted silica powder was amorphous. The broad peak at 2θ angle of 22° confirmed the amorphous nature of the silica in this study [91]. Similar properties have been reported by Kalapathy et al. [30]. This amorphous form is an advantage towards the preparation of silicon-based materials, because silica is rendered active in its amorphous form [91].

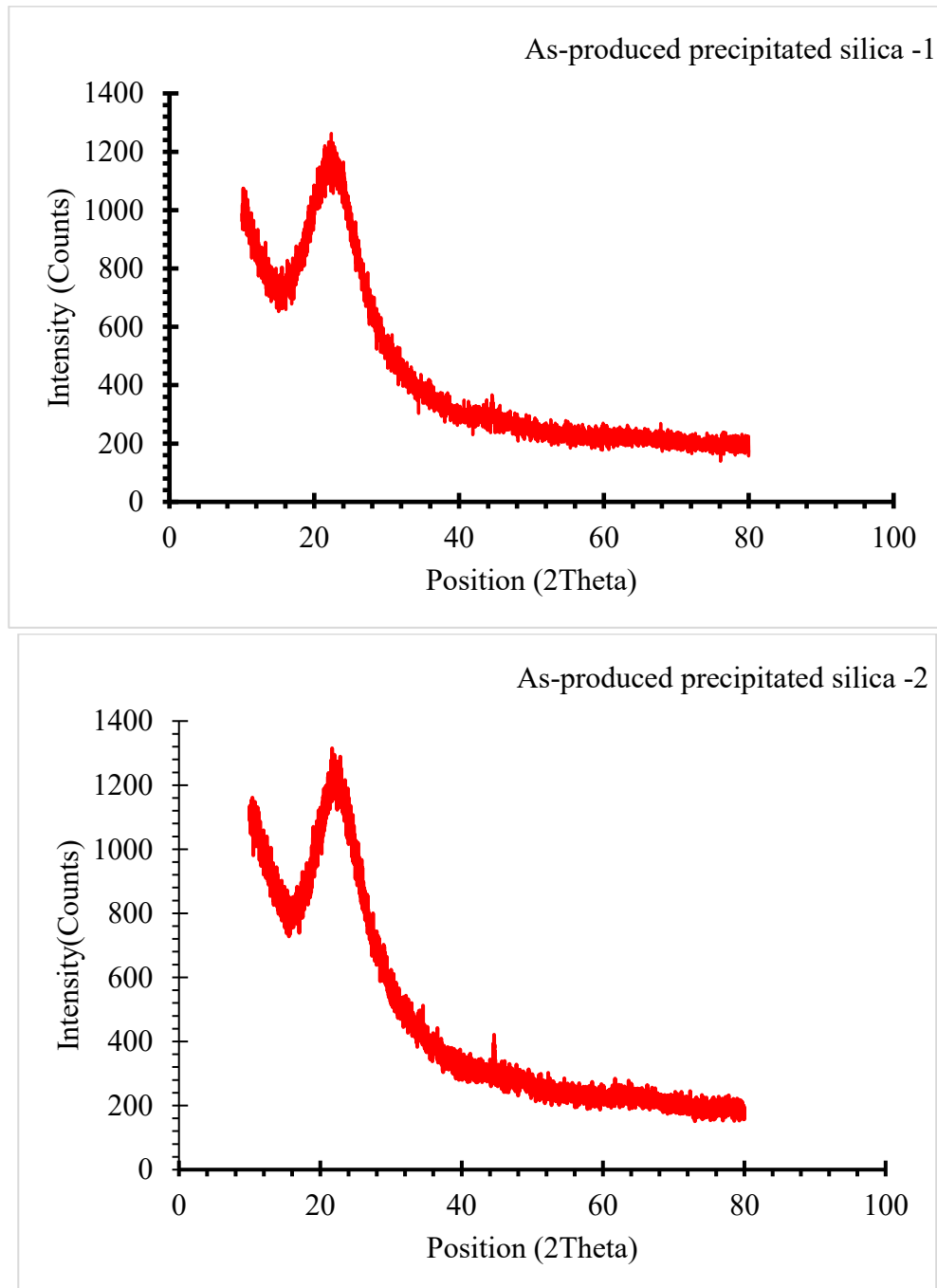


Fig. 4.17 XRD patterns of the as produced precipitated silica from rice husk ash.

During the aging period, the silicate species were gradually crystallized in order to form siloxane network (Si-O-Si). The scanning micrographs of precipitated silica (Fig. 4.18) exhibited the agglomerate particles with the uniform size in a range of 0.3-0.8 μm . This is because the well-organized assembly of silicate ions reacted with the cationic template in adequate crystallization.

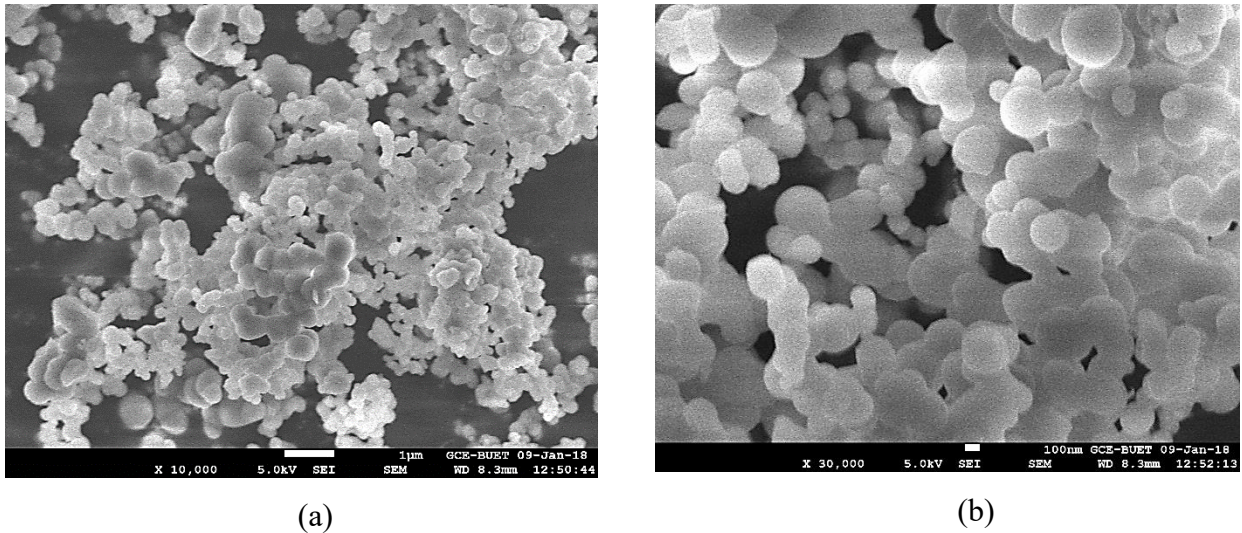


Fig. 4.18 FE-SEM images of precipitated silica at different magnifications (a) FESEM images of precipitated silica (1 μm ; X 10000); (b) FESEM images of precipitated silica (100 nm; X 30000).

The chemical composition of as produces precipitated silica has been identified to be mainly silica (SiO_2). Since it is well known fact that the submicron silica particles can be a potential health hazard [65], especially when in crystalline form, particle size analysis was necessary to determine the size distribution of the precipitated silica material for both safety and process design in terms of material handling considerations. The cumulative particle size distribution of the as-produced precipitated silica is shown in Table 4.7.

Table 4.7: Particle size analysis of as- produced precipitated silica from rice husk ash

Sample ID	Particle Size d_{10} (μm)	Particle Size d_{50} (μm)	Particle Size d_{90} (μm)
As-produced silica-1	2.5	9.9	14.1
As-produced silica-2	2.5	11	17.5

The particle size distribution shows that 90 vol% (d_{90}) is as-produced silica-1 and 2 is 14.1 μm and 17.5 μm respectively, 50 vol% (d_{50}) 9.9 μm and 11 μm and 10 vol% (d_{10}) is 2.5 μm each

sample. It can be seen that further grinding or milling of this material will readily bring it to submicron particle size distributions.

The XRF analysis of three batches of precipitated silica produced in this research work is shown in the following Table 4.8.

Table 4.8: XRF analysis of as-produced precipitated silica from rice husk ash

Chemical Composition	RHA- Silica Experiment# 01	RHA- Silica Experiment# 02	RHA- Silica Experiment# 03
	wt. (%)	wt. (%)	wt. (%)
SiO ₂	97.15 %	97.58 %	98.48 %
Na ₂ O	1.64 %	0.98 %	0.54 %
SO ₃	0.53 %	0.62 %	----
Al ₂ O ₃	0.31 %	0.29 %	0.33 %
CaO	0.14 %	0.30 %	0.29 %
Fe ₂ O ₃	0.09 %	0.09 %	0.06 %
K ₂ O	0.08 %	---	0.05 %
MgO	0.04 %	0.11 %	0.11 %
P ₂ O ₅	0.014 %	0.017 %	0.009 %
MnO	0.005 %	0.003 %	0.005 %
ZnO	0.004 %	0.005 %	0.006 %

The only difference between rice husk ash-silica experiment #1, #2 and #3 is the method of post leaching rinsing or washing. With rice husk ash silica experiment #1 and #2, the leached residue was retained on the filter paper and continuously washed with flowing warm de-ionized water until near neutral pH. In the case of rice husk ash-silica experiment #3, the leached residue was rinsed with warm deionized water to a volume approximately equal to the original leach solution volume.

The result showed in Table 4.8 depicted precipitated silica from rice husk ash- experiment #3 to have relatively high silica content and low impurities when compared to the analysis of the other two experiment. One possible explanation to this observation is that when the rice husk ash is leached with warm di-ionized water of approximately equal volume HCl solution, a neutral pH is reached quickly which results in the hydrolysis of oxide ions into soluble hydroxide. The insoluble salt adheres to silica particles is then retained during filtration. Thus, it is better to maintain a slightly acidic medium during the rinsing action after leaching [92].

CHAPTER FIVE
PRODUCTION COST ANALYSIS

5. PRODUCTION COST ANALYSIS

Bangladesh is the world sixth largest rice producer and one of the highest per capital consumer of rice (about 170 kg annually). To meet up the demand, presently there are more than 20,000 rice mills operating in Bangladesh, those are husking and preparing about 30 million metric tons of rice annually [93]. So, about 6 million metric ton of rice husk is generating every year from rice mills [93].

Burning rice husks as a fuel to generate heat for boiling rice resulting rice husk ash. About 1 million tons of rice husk ash are now generating annually, those are using for landfill and keep in open environment which causes serious environmental problem. With large silica content in the ash (80% - 95%) it becomes economical to extract silica from the ash. Due to local availability and cheap price of rice husk ash and other raw materials like, commercial grade caustic soda, HCl, sulphuric acid makes this process more cost effective than any other conventional process to manufacture high purity precipitated silica.

The cost of production includes cost of all consumable raw materials and energy used in the process. Table 5.1 gives an estimate of these costs and also gives cost comparison with conventional processes.

Table 5.1: Cost analysis of different methods of producing precipitated silica

Particulars	Existing sand process [94]	Existing RHA process [95]	Our method
	Cost BDT/kg of silica	Cost BDT/kg of silica	Cost BDT/kg of silica
Raw Material	40.00	38.00	35.00
Power cost @ BDT 9.2/Kwh	6.00	6.00	6.00
Thermal energy cost	3.00	2.50	2.00
TOTAL	49.00	46.50	43.00

This process for generation of precipitated silica has been developed from rice husk ash, which can be used for commercial exploitation. This not only impact economic and industrial sector in Bangladesh, but also solves the disposal problems of the ash.

CHAPTER SIX
SUMMARY, CONCLUSIONS AND FUTURE
WORK

6. SUMMARY, CONCLUSIONS AND FUTURE WORK

6.1 Summary and Conclusions

The feasibility of producing high purity precipitated silica from rice husk ash has been studied in this work. The rice husk ash originally collected from local automatic rice mills was combusted in different types of solid fuel steam boilers preferably FBC boiler to yield a whitish/greyish colored rice husk ash (RHA). The rice husk ash after initial characterization was subjected to a purification treatment of leaching and hot water washing. The purified rice husk ash was then digested with NaOH in predetermined weight ratios and specified temperature and pressure to prepare liquid sodium silicate. The silica content of sodium silicate was then precipitated by neutralizing sodium silicate solution using sulphuric acid. Sulphuric acid was added very slowly until acidic conditions is reached. The acidic condition indicates complete precipitation of silica from sodium silicate. A white precipitate of silica in solution of sodium sulphate was obtained. The silica obtained was filtered and sodium sulfate was removed by proper rinsing of silica by warm deionized water. The following conclusions can be drawn based on the studies carried out in this research to achieve high purity precipitated silica from locally available rice husk ash:

- It is feasible to synthesize precipitated silica of high purity from rice husk ash. The processing steps followed in this study have constituted an integrated process for producing precipitated silica from rice husk ash with reasonably high purity.
- The purity of rice husk ash in terms of silica content can be improved by leaching in hydrochloric acid followed by rinsing with warm di-ionized water. An equal volume of hydrochloric acid and warm deionized water was maintained for leaching.
- 2M HCL solution was found to be a better leaching agent for rice husk ash leaching treatment.
- Initial charge composition in terms of percent of sodium hydroxide (NaOH) was found to influence the yield of silica upon digestion in specific temperature and pressure. Increased amount of silica was achieved with higher or lower change of NaOH.
- The optimum range of the ratio of rice husk ash and sodium hydroxide was from 0.3 to 0.4 and molarity of the alkaline solution was 1.25 M to 1.67 M.

- Temperature of digestion was kept constant at 150°C, reaction period was 3 hours and the ratio of rice husk ash and water was 1:6.
- Precipitated silica was prepared by acidification of the sodium silicate stock solution with sulphuric acid followed by filtration, washing, drying at 120-150°C, followed by powdering to the desired size and bulk density.
- The silica was precipitated by adding diluted sulphuric acid to the filtered alkaline silicate solution at room temperature to 100°C.
- The yield of precipitated silica was up to 68% of the amount of silica present in the initial rice husk ash.

6.2 Future Work

The present work has been focused on manufacturing of precipitated silica from rice husk ash using laboratory facilities. The following recommendations are suggested for any further research in this area:

- Further bench work using the suggested integrated process flowsheet as a platform will be needed to establish the range of attainable RH-Silica purity from relatively from large batch samples. Such future work may provide useful information as to whether or not there is a correlation between the size of the charge to the process and the purity of the rice husk ash- Silica obtained. This will prove useful information when considering scalability of the process.
- Future work will also be needed to establish the commercial feasible route for synthesis of different grades of precipitated silica and silica gel or novel techniques that can remove more reactive impurities contained in the rice husk ash-Silica.
- This research tried successfully to explore cost-effective synthesis of high purity precipitated silica using rice husk ash. More detailed economic evaluation of this process may be focused.

REFERENCES

- [1] Goodyear Newsroom. (2018). *Goodyear Rice Husk Silica Renewable materials technology*. [online] Available at: <http://news.goodyear.eu/images-and-videos/video/goodyear-rice-husk-silica-renewable-materials-technology/a/338a6d82-4438-42c8-afbd-3df63522c080> [Accessed 09 Jan. 2018].
- [2] Fox Business. (2018). *Goodyear sees ash from rice husks as an opportunity to make tire tread production greener*. [online] Available at: <http://www.foxbusiness.com/markets/goodyear-sees-ash-from-rice-husks-as-an-opportunity-to-make-tire-tread-production-greener> [Accessed 15 Jan. 2018].
- [3] Corporate.goodyear.com. (2018). *Goodyear Reaches Supply Agreements for Rice Husk Ash Silica*. [online] Available at: <https://corporate.goodyear.com/en-US/media/news/goodyear-reaches-supply-agreements.html> [Accessed 11 Jan. 2018].
- [4] K. Srivastava, N. Shringi, V. Devra, and A. Rani, "Pure Silica Extraction from Perlite: Its Characterization and Affecting factors," *International Journal of Innovative Research in Science, Engineering and Technology*, vol. 2, pp. 2936-2942, 2013.
- [5] I. J. Fernandes, D. Calheiro, F. A. L. Sánchez, A. L. D. Camacho, T. L. A. d. C. Rocha, C. A. M. Moraes, *et al.*, "Characterization of Silica Produced from Rice Husk Ash: Comparison of Purification and Processing Methods," *Materials Research*, vol. 20, pp. 512-518, 2017.
- [6] R. K. Iler, *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica*: Wiley, 1979.
- [7] Haikudeck.com. (2018). *sodium and silicon*. [online] Available at: <https://www.haikudeck.com/sodium-and-silicon-science-and-technology-presentation-Eq7O2ojs2l#slide0> [Accessed 25 Jan. 2018].
- [8] A. S. Dimitrov, T. Miwa, and K. Nagayama, "A Comparison between the Optical Properties of Amorphous and Crystalline Monolayers of Silica Particles," *Langmuir*, vol. 15, pp. 5257-5264, 1999/08/01 1999.
- [9] ScienceStruck. (2018). *Properties of Silicon Dioxide*. [online] Available at: <https://sciencestruck.com/properties-of-silicon-dioxide> [Accessed 8 Feb. 2018].
- [10] "Chapter 5 - Silica — A Deceitful Simplicity," In *Developments in Geochemistry*. vol. 10, B. Mysen and P. Richet, Eds., ed: Elsevier, 2005, pp. 131-168.

- [11] J. D. Plummer, *Silicon VLSI technology : fundamentals, practice, and modeling*. Upper Saddle River, N.J. ; London : Prentice Hall, c2000. .
- [12] Quartzpage.de. (2018). *The Quartz Page: Chemical Properties*. [online] Available at: http://www.quartzpage.de/gen_chem.html#FI [Accessed 7 Feb. 2018].
- [13] P. S. Haus R, Priess C. , "A direct comparison of processing methods of high purity rice husk silica. ," *Asian Journal of Scientific Research*, vol. 6, pp. 573-580, 2013.
- [14] X. Ma, B. Zhou, W. Gao, Y. Qu, L. Wang, Z. Wang, *et al.*, "A recyclable method for production of pure silica from rice hull ash," *Powder technology*, vol. 217, pp. 497-501, 2012.
- [15] D. S. Jung, M. H. Ryou, Y. J. Sung, S. B. Park, and J. W. Choi, "Recycling rice husks for high-capacity lithium battery anodes," *Proc Natl Acad Sci U S A*, vol. 110, pp. 12229-34, Jul 23 2013.
- [16] E. R. Cruz-Chu, A. Aksimentiev, and K. Schulten, "Water–Silica Force Field for Simulating Nanodevices," *The Journal of Physical Chemistry B*, vol. 110, pp. 21497-21508, 2006/11/01 2006.
- [17] L. Zemnukhova, A. Egorov, G. Fedorishcheva, N. Barinov, T. Sokol'nitskaya, and A. Botsul, "Properties of amorphous silica produced from rice and oat processing waste," *Inorganic Materials*, vol. 42, pp. 24-29, 2006.
- [18] A. A. Christy, "The nature of silanol groups on the surfaces of silica, modified silica and some silica based materials," Faculty of Engineering and Science, Department of Science, University of Agder, 2014.
- [19] N. Ikram and M. Akhter, "X-ray diffraction analysis of silicon prepared from rice husk ash," *Journal of materials science*, vol. 23, pp. 2379-2381, 1988.
- [20] Anten Chemical Co., L. (2018). *Structure of precipitated silica-Anten Chemical Co., Ltd.* [online] Antenchem.com. Available at: <http://www.antenchem.com/en/news/silicas-technology/structureofprecipitatedsilica.html> [Accessed 15 Feb. 2018].
- [21] A. A. Christy, "The nature of silanol groups on the surfaces of silica, modified silica and some silica based materials," Faculty of Engineering and Science, Department of Science, University of Agder, 2014.
- [22] J. D. B. Curll, "Manufacture of silicates," ed: Google Patents, 1941.

- [23] E. L. Foletto, E. Gratieri, L. H. d. Oliveira, and S. L. Jahn, "Conversion of rice hull ash into soluble sodium silicate," *Materials Research*, vol. 9, pp. 335-338, 2006.
- [24] N. F.-V. a. L. S. S. Musić, "Precipitation of amorphous SiO₂ particles and their properties " *Brazilian Journal of Chemical Engineering* vol. 28, pp. 89-94, January-March 2011.
- [25] S. Sankar, S. K. Sharma, N. Kaur, B. Lee, D. Y. Kim, S. Lee, *et al.*, "Biogenerated silica nanoparticles synthesized from sticky, red, and brown rice husk ashes by a chemical method," *Ceramics International*, vol. 42, pp. 4875-4885, 2016/03/01/ 2016.
- [26] R. A. Bakar, R. Yahya, and S. N. Gan, "Production of High Purity Amorphous Silica from Rice Husk," *Procedia Chemistry*, vol. 19, pp. 189-195, 2016/01/01/ 2016.
- [27] T.-H. Liou and C.-C. Yang, "Synthesis and surface characteristics of nanosilica produced from alkali-extracted rice husk ash," *Materials Science and Engineering: B*, vol. 176, pp. 521-529, 2011/04/25/ 2011.
- [28] A. d. A. Fernandes, "Synthesis of Zeolites and Wollastonite from the husk ash of rice," Nuclear Technology - Materials Institute of Energy and Nuclear Research 2007.
- [29] N. S. Yalçın, V., "Studies on silica obtained from rice husk," *Ceramics International*, vol. 27, pp. 219-224, 2001.
- [30] U. Kalapathy, A. Proctor, and J. Shultz, "A simple method for production of pure silica from rice hull ash," *Bioresource Technology*, vol. 73, pp. 257-262, 2000/07/01/ 2000.
- [31] R. Conradt, P. Pimkhaokham, and U. Leela-Adisorn, "Nano-structured silica from rice husk," *Journal of Non-Crystalline Solids*, vol. 145, pp. 75-79, 1992/01/01/ 1992.
- [32] H. Riveros and C. Garza, "Rice husks as a source of high purity silica," *Journal of Crystal Growth*, vol. 75, pp. 126-131, 1986/05/01/ 1986.
- [33] N. Yalçın and V. Sevinç, "Studies on silica obtained from rice husk," *Ceramics International*, vol. 27, pp. 219-224, 2001/01/01/ 2001.
- [34] N. I. Rahizuwan Hamid, "Effect of Grinding on Workability and Strength of Penang Rice Husk Ash Blended Concrete Grade 30," *The Institution of Engineers, Malaysia*, vol. 76, pp. 47-51, 1 July 2015.
- [35] J. H. Bates, S. S. Wagers, R. J. Norton, L. M. Rinaldi, and C. G. Irvin, "Hydrolysis of cations," in *Inorganic Complexes*, 1976.

- [36] Laccei.org. (2006). *Marine Durability Characteristics of Rice Husk Ash-Modified Reinforced Concrete*. [online] Available at: http://www.laccei.org/LACCEI2006-PuertoRico/Papers%20-pdf/MAT050_Reddy.pdf [Accessed 18 Feb. 2018].
- [37] N. a. F. Bouzoubaa. (2001) Concrete Incorporating Rice-Husk Ash: Compressive Strength and Chloride-Ion Penetrability, International Centre for Sustainable Development of Cement and Concrete (ICON). *Natural Resources Canada*.
- [38] T. Watari, A. Nakata, Y. Kiba, T. Torikai, and M. Yada, "Fabrication of porous SiO₂/C composite from rice husks," *Journal of the European Ceramic Society*, vol. 26, pp. 797-801, 2006/01/01/ 2006.
- [39] Market, P. (2018). *Precipitated Silica Market by End-Use Industry & Application - Global Forecast 2021 | MarketsandMarkets*. [online] Marketsandmarkets.com. Available at: <https://www.marketsandmarkets.com/Market-Reports/precipitated-silica-market-248726425.html> [Accessed 27 Feb. 2018].
- [40] Reportbuyer.com. (2016). *Precipitated Silica Market by End-Use Industry , by Application , & by Region - Global Forecast to 2021* Available: <https://www.prnewswire.com/news-releases/precipitated-silica-market-by-end-use-industry--by-application---by-region---global-forecast-to-2021-300313705.html> [Accessed 09 March. 2018]
- [41] G. V. Research. Specialty Silica Market Size, Share & Trend Analysis Report By Product (Precipitated Silica, Silica Gel, Fused Silica), By Application (Rubber, Food & Healthcare, Coatings), And Segment Forecasts, 2012 - 2022 [Online]. Available: <https://www.grandviewresearch.com/industry-analysis/specialty-silica-market> [Accessed 09 March. 2018]
- [42] Z. T. P. Ltd. Analysis of Export of precipitated silica [Online]. Available: <https://www.zauba.com/exportanalysis-precipitated+silica+silicon-report.html> [Accessed 10 March. 2018]
- [43] T. M. Research. Precipitated Silica Market - Global Industry Analysis, Size, Share, Growth, Trends and Forecast 2015 - 2023 [Online]. Available: <https://www.transparencymarketresearch.com/precipitated-silica-market.html> [Accessed 12 March. 2018]
- [44] Precipitatedsilica.net. (2018). *Supersil Precipitated Silica, Supersil 220 Silica, Micronized Silica, Precipitated Silica Powder, Mumbai, India*. [online] Available at: <http://www.precipitatedsilica.net/applications.html> [Accessed 12 March. 2018].
- [46] P. Maestro, Y. Bomal, and T. Chopin, "Nanoparticles in chemistry and their industrial applications," in *NSTI Nanotechnology Conference and Trade Show*, 2006.

- [47] Y. Nakata, M. Suzuki, T. Okutani, M. Kikuchi, and T. Akiyama, "Preparation and Properties of SiO₂ from Rice Hulls," *Journal of the Ceramic Society of Japan*, vol. 97, pp. 842-849, 1989.
- [48] E. Natarajan, "Pyrolysis of rice husk in a fixed bed reactor," 2009.
- [49] S. Chandrasekhar, P. Pramada, and L. Praveen, "Effect of organic acid treatment on the properties of rice husk silica," *Journal of Materials Science*, vol. 40, pp. 6535-6544, 2005.
- [50] A. Proctor, "X-ray diffraction and scanning electron microscope studies of processed rice hull silica," *Journal of the American Oil Chemists' Society*, vol. 67, pp. 576-584, 1990.
- [51] C. Real, M. D. Alcala, and J. M. Criado, "Preparation of silica from rice husks," *Journal of the American ceramic society*, vol. 79, pp. 2012-2016, 1996.
- [52] H. Kurama and S. Kurama, "The effect of chemical treatment on the production of active silica from rice husk," in *18th international mining congress and exhibition of Turkey-IMCET*, 2003.
- [53] M. Patel, A. Karera, and P. Prasanna, "Effect of thermal and chemical treatments on carbon and silica contents in rice husk," *Journal of Materials Science*, vol. 22, pp. 2457-2464, 1987.
- [54] A. Chakraverty, P. Mishra, and H. Banerjee, "Investigation of combustion of raw and acid-leached rice husk for production of pure amorphous white silica," *Journal of Materials Science*, vol. 23, pp. 21-24, 1988.
- [55] A. Chakraverty, H. Banerjee, and P. Mishra, "Production of amorphous silica from rice husk in a vertical furnace," *AMA, Agricultural Mechanization in Asia, Africa and Latin America*, vol. 21, pp. 69-75, 1990.
- [56] J. Umeda and K. Kondoh, "High-purification of amorphous silica originated from rice husks by combination of polysaccharide hydrolysis and metallic impurities removal," *Industrial crops and products*, vol. 32, pp. 539-544, 2010.
- [57] P. Sidheswaran and A. Bhat, "Recovery of amorphous silica in pure form from rice husk," *Transactions of the Indian Ceramic Society*, vol. 55, pp. 93-96, 1996.
- [58] J. Anzelmo, A. Seyfarth, and L. Arias, "Approaching a universal sample preparation method for XRF analysis of powder materials," *Adv. X-ray Anal*, vol. 44, pp. 368-373, 2001.

- [59] M. S. Shackley, "An introduction to X-ray fluorescence (XRF) analysis in archaeology," in *X-ray fluorescence spectrometry (XRF) in geoarchaeology*, ed: Springer, 2011, pp. 7-44.
- [60] A. Loupilov, A. Sokolov, and V. Gostilo, "X-ray Peltier cooled detectors for X-ray fluorescence analysis," *Radiation Physics and Chemistry*, vol. 61, pp. 463-464, 2001.
- [61] V. S. Ramachandran and J. J. Beaudoin, *Handbook of analytical techniques in concrete science and technology: principles, techniques and applications*: Elsevier, 2000.
- [62] U. Kalapathy, A. Proctor, and J. Shultz, "An improved method for production of silica from rice hull ash," *Bioresource technology*, vol. 85, pp. 285-289, 2002.
- [63] S. Genieva, S. Turmanova, A. Dimitrova, and L. Vlaev, "Characterization of rice husks and the products of its thermal degradation in air or nitrogen atmosphere," *Journal of Thermal Analysis and Calorimetry*, vol. 93, pp. 387-396, 2008.
- [64] D. F. Houston, "Rice: Chemistry and Technology," American Association of Cereal Chemists 1972.
- [65] Y. Shinohara and N. Kohyama, "Quantitative analysis of tridymite and cristobalite crystallized in rice husk ash by heating," *Industrial Health*, vol. 42, pp. 277-285, 2004.
- [66] D. Singh, R. Kumar, A. Kumar, and K. Rai, "Synthesis and characterization of rice husk silica, silica-carbon composite and H₃PO₄ activated silica," *Cerâmica*, vol. 54, pp. 203-212, 2008.
- [67] S. Traoré, D. Traoré, S. Kourouma, and S. Magassouba, "Preparation of Silicon from Rice Husk as Renewable Energy Resource by the Use of Microwave Ashing and Acid Digestion," *International Journal of Energy Engineering*, vol. 8, pp. 25-29, 2018.
- [68] N. Yalcin and V. Sevinc, "Studies on silica obtained from rice husk," *Ceramics international*, vol. 27, pp. 219-224, 2001.
- [69] N. Nayak and C. R. Panda, "Aluminium extraction and leaching characteristics of Talcher Thermal Power Station fly ash with sulphuric acid," *Fuel*, vol. 89, pp. 53-58, 2010.
- [70] S. Shcherban, I. Pevzner, and V. Rayzman, "Technologies of coal fly ash processing into metallurgical and silicate chemical products," American Chemical Society, Washington, DC (United States) 1995.

- [71] A. Seidel, A. Sluszny, G. Shelef, and Y. Zimmels, "Self inhibition of aluminum leaching from coal fly ash by sulfuric acid," *Chemical Engineering Journal*, vol. 72, pp. 195-207, 1999.
- [72] O. Levenspiel, "Chemical reaction engineering," 1962.
- [73] M. E. Wadsworth and H. Y. Sohn, *Rate processes of extractive metallurgy*. New York: Plenum Press, 1979.
- [74] V. Yadav, T. Sharma, and V. Saxena, "Dissolution kinetics of potassium from glauconitic sandstone in acid lixiviant," *International Journal of Mineral Processing*, vol. 60, pp. 15-36, 2000.
- [75] L. Hunt, J. Dismukes, J. Amick, A. Schei, and K. Larsen, "Rice hulls as a raw material for producing silicon," *Journal of the Electrochemical Society*, vol. 131, pp. 1683-1686, 1984.
- [76] R. B. Warjri, "Sol-gel synthesis of glass-ceramics using rice husk ash and its gelcasting," 2010.
- [77] M. Fleury, O. Sissmann, E. Brosse, and M. Chardin, "A Silicate Based Process for Plugging the Near Well Bore Formation," *Energy Procedia*, vol. 114, pp. 4172-4187, 2017.
- [78] A. A. Hamouda and H. A. A. Amiri, "Factors affecting alkaline sodium silicate gelation for in-depth reservoir profile modification," *Energies*, vol. 7, pp. 568-590, 2014.
- [79] T. An-Peng, "A theory of polymerization of silicic acid," *Scientia Sinica*, vol. 12, pp. 1311-1320, 1963.
- [80] H. A. A. Amiri, "Evaluation of Alkaline Sodium Silicate Gel for Reservoir In-Depth Profile Modifications to Enhance Water Sweep Efficiency in Sandstone Reservoirs," 2014.
- [81] K. R. Iler, "The chemistry of silica," *Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica*, 1979.
- [82] P. Krumrine and S. Boyce, "Profile modification and water control with silica gel-based systems," in *SPE Oilfield and Geothermal Chemistry Symposium*, 1985.
- [83] M. Hessien, M. Rashad, R. Zaky, E. Abdel-Aal, and K. El-Barawy, "Controlling the synthesis conditions for silica nanosphere from semi-burned rice straw," *Materials science and engineering: B*, vol. 162, pp. 14-21, 2009.

- [84] M.-J. Muñoz-Aguado and M. Gregorkiewitz, "Sol-gel synthesis of microporous amorphous silica from purely inorganic precursors," *Journal of colloid and interface science*, vol. 185, pp. 459-465, 1997.
- [85] J. Jurinak, L. Summers, and K. Bennett, "Laboratory testing of colloidal silica gel for oilfield applications," *J. SPE Prod. Eng*, vol. 6, pp. 406-412, 1991.
- [86] C. J. Brinker and G. W. Scherer, *Sol-gel science: the physics and chemistry of sol-gel processing*: Academic press, 2013.
- [87] J. Zha and H. Roggendorf, "Sol-gel science, the physics and chemistry of sol-gel processing, Ed. by CJ Brinker and GW Scherer, Academic Press, Boston 1990, xiv, 908 pp., bound—ISBN 0-12-134970-5," *Advanced Materials*, vol. 3, pp. 522-522, 1991.
- [88] K. Quarch and M. Kind, "Inorganic precipitated silica gel. Part 1: Gelation kinetics and gel properties," *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, vol. 33, pp. 1034-1039, 2010.
- [89] B. Vinot, R. Schechter, and L. W. Lake, "Formation of water-soluble silicate gels by the hydrolysis of a diester of dicarboxylic acid solublized as microemulsions," *SPE Reservoir Engineering*, vol. 4, pp. 391-397, 1989.
- [90] T. Ponomareva, S. Kontorovich, M. Chekanov, and E. Shchukin, "Kinetics of shrinkage during formation of polysilicic acid hydrogel structures," vol. 46, ed: PLENUM PUBL CORP CONSULTANTS BUREAU, 233 SPRING ST, NEW YORK, NY 10013, 1984, pp. 118-120.
- [91] J. Payá, J. Monzó, M. Borrachero, A. Mellado, and L. Ordoñez, "Determination of amorphous silica in rice husk ash by a rapid analytical method," *Cement and Concrete Research*, vol. 31, pp. 227-231, 2001.
- [92] W. Xu, J. Wei, J. Chen, B. Zhang, P. Xu, J. Ren, *et al.*, "Comparative Study of Water-Leaching and Acid-Leaching Pretreatment on the Thermal Stability and Reactivity of Biomass Silica for Viability as a Pozzolanic Additive in Cement," *Materials*, vol. 11, p. 1697, 2018.
- [93] IDLC Finance Limited (2014). *IDLC Monthly Business Review*. Rice Milling in Bangladesh. [online] Dhaka: IDLC. Available at: <http://idlc.com/public/.../Monthly%20Business%20Review%20-%20December%202014.pdf> [Accessed 15 Jan. 2018].

- [94] Isernia, G. (2018). *GLASS SERVICE - Solutions For The Glass Industry - Home*. [online] Glassservice.it. Available at: <https://www.glassservice.it/> [Accessed 20 May 2018].
- [95] Services, N. (2018). *Silica From Rice Husk Ash - Manufacturing Plant, Detailed Project Report, Profile, Business Plan, Industry Trends, Market Research, Survey, Manufacturing Process, Machinery, Raw Materials, Feasibility Study, Investment Opportunities, Cost And Revenue in Project Reports & Profiles*. [online] NIIR Project Consultancy Services. Available at: <https://www.niir.org/profile-project-reports/profile/2179/silica-from-rice-husk-ash-manufacturing-plant-detailed-project-report-profile-business-plan-industry-trends-market-research-survey-manufacturing-process-machinery-raw-materials-feasibility-study-investment-opportunities-cost-revenue.html> [Accessed 12 May 2018].

