ESTABLISHING POSSIBLE MECHANISMS FOR PRODUCING NANOPARTICLES OF TRONOH SILICA SAND VIA LOW SPEED MECHANICAL MILLING PROCESS

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ABSTRACT

Silica sand is abundantly available in every part of the world and it is commonly used for production of ceramic matrix composites, construction of buildings, bridges, dams, roads and bricks as well as in production of refractory materials for high temperature furnaces. Some of the most important properties of silica sand are high hardness, high tensile and compressive strength, high chemical resistance, high temperature resistance, good insulation, high wear resistance and brittle in nature. Advanced uses of silica sand include in the production of engine, rotor, valve, bearings, sensors and thermal protection system. Natural silica sand is also found in Malaysia especially in Tronoh, Perak where previous tin mining activities were actively progressed 50 years ago. Except for housing construction foundation, there was no efforts or initiatives taken in converting the natural sand to a different particle form or size for other potential technical applications. To date, relevant literatures reported that the nanosilica particles are produced by chemical synthesis, ultrasonic technique in the hydrolysis-condensation stage by azeotropic distillation, high speed fluidized bed jet mill, high speed vertical rotating mill and planetary ball mill. There was no reported or published works related to the production of silica sand nanoparticles from the natural silica sand by using low speed of ball milling. Hence this proposed research serves as an indigenious technique for transforming silica sand to high purity silica sand nanoparticles of less than 100nm size by using low speed ball millRaw Tronoh silica sand was milled for 10 hours with heating process for every 2 hours of milling. The optimum parameters were first identified using Taguchi method of orthogonal array. Results from the experiments were analyzed using particle size analyzer and SN ratio as well as ANOVA method to determine the most significant parameters. Lab-scale production was done and the results once again analyzed using particle size analyzer to obtain the particles size and size distribution, FESEM for confirmation of nanoparticles presence and EDX for chemical composition. High purity silica sand nanoparticles with size of less than 50 nm have been repeatedly achieved in this research.

ABSTRAK

Pasir silika terdapat dengan banyaknya di setiap bahagian dunia dan ia biasanya digunakan bagi pengeluaran rencam matriks seramik, pembinaan bangunan, jambatan, empangan, jalan raya dan batu bata serta pengeluaran bahan-bahan refraktori untuk relau suhu yang tinggi. Antara sifat-sifat terpenting pasir silika adalah kekerasan yang tinggi, kekuatan tegangan dan mampatan yang tinggi, rintangan kimia yang tinggi, ketahanan suhu yang tinggi, penebat yang baik, rintangan haus yang tinggi dan rapuh secara semula jadi. Penggunaan pasir silika yang lebih maju termasuk dalam pengeluaran enjin, rotor, injap, galas, penderia dan sistem perlindungan haba. Pasir silika semulajadi juga didapati di Malaysia terutamanya di Tronoh, Perak di mana aktiviti perlombongan bijih timah giat telah berkembang 50 tahun yang lalu. Kecuali dalam pembinaan asas perumahan, tiada usaha atau inisiatif-inisiatif yang diambil dalam penukaran pasir semulajadi kepada zarah berbeza bentuk atau saiz untuk aplikasi teknikal lain yang berpotensi. Sehingga kini, kajian berkaitan melaporkan bahawa zarah-zarah silika nano yang dihasilkan adalah daripada sintesis kimia, teknik penyulingan ultrasonik di peringkat herba-pemeluwapan, pengisaran terbendalir pada kelajuan tinggi, pengisaran berputar menegak pada kelajuan tinggi dan pengisaran bola planet. Tiada kajian yang dilaporkan atau diterbitkan berkaitan dengan pengeluaran pasir silika nano daripada pasir silika semulajadi dengan menggunakan pengisaran bola berkelajuan rendah. Oleh itu kajian ini berfungsi sebagai satu teknik perintis untuk merubah pasir silika menjadi pasir silika nano berketulenan tinggi dengan saiz kurang daripada 100nm menggunakan pengisaran bola berkelajuan rendah. Pasir silika Tronoh mentah dikisar selama 10 jam dengan proses pemanasan bagi setiap 2 jam pengisaran. Parameter optimum dikenalpasti menggunakan kaedah Taguchi. Keputusan daripada eksperimen dianalisis menggunakan penganalisis saiz zarah dan nisbah SN sertah kaedah ANOVA diaplikasikan untuk menentukan parameter yang paling ketara. Pengeluaran skala makmal telah dilakukan dan keputusan sekali lagi dianalisis menggunakan penganalisis saiz zarah untuk mendapatkan saiz zarah dan pengagihan saiz, FESEM untuk pengesahan kehadiran partikel nano dan EDX bagi komposisi kimia. Pasir silika nano berketulenan tinggi dengan saiz kurang daripada 50 nm telah berulang kali berjaya dicapai dalam kajian ini.

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CHAPTER I

INTRODUCTION

1.1 Chapter Overview

Chapter 1 presents an introduction to the research works. This chapter contains the background of study, problem statement, research objectives, scope of research and organization of thesis.

1.2 Background of study

Silica sand is abundantly available in every part of the world. Its properties such as high hardness, chemical inertness, resistance to high temperature and stress as well as good insulator make silica sand a useful and preferred choice in variety of applications. Silica sand is commonly used in construction industry as building products, production of ceramic matrix composites, refractory materials for furnaces, glassmaking and water filtration. There is also a demand for higher purity silica sand to be used in advanced applications such as in automotive parts manufacturing, green technology and aerospace.

Silica sand resources are also found throughout Malaysia comprising largely natural sand deposits and ex-tin mine tailings. Minerals and Geoscience Department Malaysia estimated that the country has approximately 148.4 million tonnes of silica sand reserves located in the states of Johor, Perak, Terengganu, Kelantan, Sabah and Sarawak [1]. Increase in silica sand production from sand mining operations indicates the huge potential for higher quality silica sand deposits.

Nanoparticles of silica sand have been actively researched and produced due to the unique features as a result of size reduction [2]. Two major changes in physical properties are the increase in surface area to volume ratio and the particles size moving into realm where quantum effects predominate. Silica sand nanoparticles have proved to be a very effective additive to polymers by improving strength, flexibility and durability. Nanosilica can also be used as an additive to improve workability and strength of self-compacting and high-performance concretes [3].

1.3 Problem Statement

As a result of tin mining activities that was actively progressed in Tronoh, Perak 50 years ago, natural silica sand reserves are abundantly available throughout the area. Except for housing construction foundation, there are no efforts or initiatives taken to convert the natural silica sand to a different particle form or size for other potential applications.

Nanosilica particles are mostly produced by chemical processes. However, chemical synthesis of nanosilica results in high contamination in its products. As the demand is increasing for higher purity nanosilica, contamination should be kept to the minimum level. Other than chemical sysnthesis, sol-gel process, vaporization at high temperature, precipitation, high speed vertical rotating mill and planetary ball mill are among the most commonly used methods to produce silica sand nanoparticles.

There are no reported or published works related to production of silica sand nanoparticles by using low speed ball milling. Hence, this research serves as indigenous technique for transforming natural silica sand to silica sand nanoparticles.

1.4 Research Objectives

The objective of this research is to establish a technique of transforming natural Tronoh silica sand to silica sand nanoparticles by using a combination of low speed ball milling and heating processes. This research also focused on determining the optimum ball milling parameters to produce silica sand nanoparticles.

1.5 Scope of work

The research is focused on producing the silica sand nanoparticles consistently by using low speed ball milling and heating processes. Pre-milling processes such as washing, drying and sieving were done to eliminate the impurities in silica sand deposits. Parameters of the milling process were investigated to determine the optimum variables. The silica sand is milled and the time taken for the size to be reduced to nanometer region is observed. The milling process is repeated using the same silica sand deposits and milling parameters to test the ability of repetitive production of silica sand nanoparticles.

Analysis to the nanosilica produced is done particularly to determine its average particles size and particles size distribution. Confirmation of the average particles size results is proved by FESEM analysis. EDX analysis will determine the percent purity of nanosilica particles produced in this research.

1.6 Organization of Thesis

Five chapters are presented in this thesis. Chapter 1 presents the introduction to the research. The background of study, problem statement, research objectives and scope of work are included in this chapter.

Chapter 2 provides the literature review related to the research. This chapter started with the introduction to silica sand and discussed the properties as well as its applications. The definition of nanoparticles, its unique properties and uses are also presented. This chapter also discussed the various production methods of nanoparticles. The mechanisms and different types of ball milling are explained in this chapter.

Chapter 3 discussed the methodology for this research. Details of materials and equipments used are explained in this chapter. Sample preparation and parameters optimization are also discussed. The steps involved in the milling process are elaborated for further understanding. This chapter also presents the analysis performed on the outputs.

Chapter 4 presents the results and discussion for the research works done. The average particle size and particle size distribution results obtained from particle size analyzer are discussed in detail. The results from FESEM analysis are also presented in this chapter. The chemical composition results obtained from EDX analysis are discussed as well.

Chapter 5 which is the final chapter presents the conclusion and findings of the research. Recommendations for better results in future researches are also given.

1.7 Chapter Summary

This chapter presented a brief introduction to the research. Background of the study is explained to understand the production methods of silica sand nanoparticles as well as its potential applications. The unique properties of silica sand and nanoparticles are also briefly discussed in this chapter. Problem statement of the research clearly addressed the importance of this research to be carried out, followed by research objectives, scope of work and organization of thesis. In the next chapter, literature review in the topics of silica sand, nanoparticles and ball milling will be presented for fundamental understanding. Related works and research are also presented and discussed.

CHAPTER II

LITERATURE REVIEW

2.1 Chapter Overview

This chapter presents the literature review and theories of the research. It will begin with defining silica sand as well as its properties and common applications. The chapter will then proceeds with nanoparticles subtopic. The unique properties of nanoparticles, its applications and methods of production will be thoroughly discussed. Ball milling method of nanoparticles production will also be presented in this chapter. The chapter will end with a review on previous works and researches.

2.2 Silica Sand

Silica is a group of minerals which composed of silicon and oxygen, two most abundant elements in earth's crust [4]. The chemical formula for silica is SiO_2 [5]. Silica is an industrial term for sand or easily disaggregated sandstone which consists of small grains or particles of mineral and rock fragments. Silica sand contains high silica proportion usually more than 95% of SiO_2 in quartz form. Silica sand is used for various purposes other than construction [5][8]. The most common silica crystal is quartz which is also the second most common mineral on earth's surface. Quartz found in every type of rocks, igneous, metamorphic and sedimentary [1], [5].Other components are feldspar, aluminium and iron-bearing minerals [5].

Most of the products for industrial use are termed silica sand. The word "sand" describes a material with grain size distribution in the range of 0.06-2.00 millimeters. For industrial uses, silica of at least 95% to 98% SiO_2 is preferred [1][5]. Silica is found more commonly in crystalline state but also occurs in amorphous state resulting from weathering or plankton fossilization [5][9][10]. Amorphous state can converts to crystalline form at high heat [11].

Crystalline silica is abundantly available and the most commonly found natural material [12]. It is found in a variety of forms with quartz the most common while the other forms are tridymite and cristobalite [9][10]. Quartz also occurs in cryptocrystalline forms. Fibrous forms, known as chalcedony include semi-precious stone versions such as agate, onyx and carnelian. Granular varieties include jasper and flint while anhydrous forms consist of diatomite and opal [5], [12]. Amorphous is a term to describe forms that have no regular crystal structure. It has a wide range of different types with fossilized skeletal remains of marine organism is the most common [9].

Crystalline silica has many uses because of its unique physical and chemical properties. Commercially produced silica products are quartzite, tripoli, ganister, chert, and novaculite [12]. Industry mainly uses crystalline forms of silica, i.e. quartz and cristobalite [1]. Quartz is the most common crystalline form industrially used. Cristobalite, polymorph of quartz is also being used in industry. Tridymite is found in rocks but not an important industrial product [11].

2.2.1 Source of Silica Sand

Silica sand is produced from unconsolidated sands and crushing weakly cemented sandstone, further processes depend on end-use [1]-[7]. Silica sand can only be extracted from where the minerals occur and there are only a limited number of locations where extraction is considered economically feasible [6]. To be considered as potentially suitable for extraction, deposits must be capable of being worked economically and available in sufficient quantity to justify capital investment [6]. High grade of silica sand is normally found in unconsolidated deposits below thin layers of overburden. It is also found as 'veins' or quartz within other rocks. These veins can have a thickness of a few meters [1].

Silica mining is done by surface-mined in an open pit operation. Dredging and underground mining methods were also being utilized with the use of standard mining equipments [5][8]. Extracted ore undergoes further processing to increase the silica content by reducing impurities. It is then dried and sized to produce optimum particle size distribution, depending on end use [1][5]. The objectives of silica sand processing are to clean the quartz grains and increases percentage of silica content, producing the optimum size distribution and to reduce impurities especially iron and chromium.

To meet the industry's tight specifications, the sand are often subjected to extensive physical and chemical processing which involves screening, crushing and adjusting grain-size distribution, as well as removing contaminating impurities [5]. After processing, the sand may be sold in moist state or being dried. Dry grinding in rotary mills, using beach pebbles or alumina balls as grinding media is the most common way to produce silica and cristobalite flour [1].

2.2.2 Properties of Silica Sand

Silica sand is highly valued for its unique chemical and physical properties. These includes high silica content in quartz form, low levels of impurities particularly clay, iron oxides and refractory minerals such as chromite. Silica sand also has a narrow grain-size distribution (in the range of 0.5 to 0.1 mm) [7]. Silica is noncombustible, colorless or white, tasteless trigonal crystal which occurs naturally in crystalline and amorphous forms. Specific gravity and melting point of silica sand depend on the crystalline form. The basic structural unit of silica mineral is silicon tetrahedral, SiO_4. Quartz, cristobalite and tridymite are the three most common crystalline forms of free silica and can change their form under different temperature and pressure conditions. Quartz structure is more compact than tridymite or cristobalite. Quartz melts to glass and has the lowest coefficient of expansion by heat compared to any known substances. Silica is also insoluble in water and most acids but dissolves in hydroflouric acid, forming gaseous silicon tetraflouride [12].

Silica is hard, chemically inert and has a high melting point, results in strong atomic bonds. These are the prized qualities in foundries and filtration systems [1]. Industrial sand's strength, silicon dioxide contribution and non-reactive properties make it important in the production of everyday products [5]. High purity fused silica that is used by the electronics industry has at least 99.95% SiO_2, high electromagnetic radiation transparency, very low expansion coefficient and good insulation properties [8]. Industrial uses of silica sand depend on its purity and physical characteristics. The most important physical properties are grain size and distribution, sphericity, grain shape, grain strength and refractoriness [5]. Industrial sand is high purity sand with controlled sizing. It is a more precise product compared to concrete and asphalt gravels [5].

The three major crystalline silica forms, quartz, tridymite and cristobalite are stable at different temperatures. When low temperature alpha quartz is heated at atmospheric pressure, it changes to beta quartz at 573°C. At 870°C, tridymite is formed while cristobalite is formed at 1470°C. The melting point of silica is 1610°C, higher than iron, copper and aluminium. This is the reason why it is used to produce moulds and cores for metal castings production [5].

2.2.3 Silica Sand Processing

Silica sand processing varies in degrees and complexity depends on the end use of the sand. Most operations processing involves attrition scrubbing, washing and size classification to remove coarse and very fine fractions as well as to obtain clean sand with the desired particle size distribution. Most of the foundry sands have to be supplied dried and drying facilities are a substantial capital investment. Selected grades of silica sand are coated with resin binders to produce high value-added product. Wide ranges of grades produced are usually based on different particle sizes and resin types. Some silica sand is calcined to convert quartz to cristobalite. Cristobalite is a higher temperature form of silica and more suitable to be use in ceramics. Both cristobalite and dried silica sand are finely milled to produce various silica flour grades [7].

Cleaning quartz grains and increasing silica content is achieved by washing to remove the clay minerals and scrubbing by attrition between particles. Production of optimum size distribution is done by screening to remove unwanted coarse particles and classification in upward current of water to remove unwanted fine material. Quartz grains are often iron stained and staining may be removed or reduced by chemical reaction using sulphuric acid at different temperatures. Impurities present as separate mineral particles may be removed by using techniques such as gravity separation, froth flotation and magnetic separation. For highest purity, especially for electronics applications, extra cleaning with aggressive acids such as hydroflouric acid combined with thermal shock may be necessary. After processing, the sand is dried and some applications require it to be ground in ball mills to produce very fine material, called silica flour. Quartz may be converted to cristobalite in rotary kiln at high temperature, with the assistance of catalyst. Some specialist applications require the quartz to be melted in electric arc furnaces, followed by cooling and grinding processes to produce fused silica [5].

2.2.4 Applications of Silica Sand

Historically, the most important market for silica sand is foundry casting [7]. It is also an essential raw material for glassmaking as well as chemicals manufacture, ceramics and water filtration industry [6]. There is a requirement and demand for higher quality silica sand to be used in critical areas such as military, aerospace and precision automotive parts. Demand for glass sand has also increased throughout recent years [7].

2.2.4.1 Foundry and Metal Casting

Silica sand is used as the main mould and core making material for ferrous and non-ferrous castings. Lower purity sand is added to clay, forming molds for aluminium, casting iron and copper alloys [12]. In the past, naturally-bonded molding sands were widely used but today, the demand is mostly for clay-free (washed) sands which are high in silica content. Binding agent, either clay (usually bentonite) or a chemical, such as resin is added to the sand [7]. Crystalline silica has higher melting point than iron, copper and aluminium. Castings can be produced by pouring molten metal into moulds made of silica sand and binder. Silica's high fusion point (1760°C) and low thermal expansion produce stable cores and moulds which are compatible with pouring temperatures and alloy systems. Its chemical purity prevents interaction with catalysts or the curing rate of chemical binders [5]. Quartz and cristobalite are main the components in investment casting (also called precision casting) for production of specialist products such as dental bridges, jewellery, aviation turbines and golf clubs [1].

2.2.4.2 Electronic and optical components

Quartz has a high demands for pure quartz crystals from. High-purity synthetic and natural quartz crystals are used for special optical applications such as fiber optics and in manufacture of microcomputers, television equipments, watches and wireless communications equipments. Optical grade quartz is used to make lenses and windows in lasers and other devices [12].

2.2.4.3 Glassmaking

Silica sand is a primary component of all types of standard and specialty glasses. It provides the essential SiO_2 components and its chemical purity determines the colour, clarity and strength. It is also used in production of flat glass for building and automotive use, jar glass for foods and beverages, and tableware. In pulverized form, it is used for production of fiberglass insulation and reinforcing glass fibers [5]. Glass fibers, used for composite reinforcement or in decorative textiles, are both made from fine ground flour silica [1][8][12]. Most of the commercial glasses in our everyday uses are soda-lime-silica glasses, containing 70-74 % silica (SiO_2). The source mainly silica sand, although silica is also being recovered from recycled glass which is known as cullet. Manufacture of glass also requires addition of other industrial minerals such as dolomite, limestone, feldspar and salt [7].

2.2.4.4 Metallurgical

In metal production, silica sand operates as a flux to lower the melting point and viscosity of slag to make them more reactive and efficient. Copper and zinc at some smelter uses sand as fluxing agent, which in molten state reacts with impurities in the ore and produces a slag. The slag is drawn off with impurities, leaving refined metal behind [5][8]. Lump silica is used alone or with lime to achieve the desired base/acid ratio required for purification purpose. These base metals can be further refined and modified to achieve specific properties such as corrosion resistance, high strength or electrical conductivity. Silica sand is also being used by steel and foundry industries for de-oxidation and grain refinement processes [5]. Quartz is the raw material for production of silicon metal and ferrosilicon. Silicon metal is used in the production of alloys based on copper, aluminium and nickel. Ferrosilicon is a major alloying ingredient to form iron and steel. Metal ores purified in furnace by silica sand are transformed into metal slag [1].

2.2.4.5 Chemical production

SiO_2 is reduced to silicon metal by coke in arc furnace to produce Si precursor of chemical processes. Industrial sand is the main component in chemicals such as silicon tetrachloride, sodium silicate and silicon gels. These chemicals are used in household and industrial cleaners, to manufacture fiber optics and also removing impurities from cooking oil and brewed beverages [5][8]. Cristobalite and high purity quartz are used to produce silicon chemicals including silica gel, sodium silicate, silicones, tetrachloride, silicon silanes and pure silicon. Pure silicon is used for production of silicon chips. Silicon products are used in pharmaceuticals, detergents, and cosmetics [1].

2.2.4.6 Building products

Industrial sand is the primary structural components in most of building and construction products. Whole grain silica is used in flooring and rendering compounds, mortars, silica and aerated concrete blocks, white line markings, glues for roof, specialty cements, roofing shingle, stucco, resin injection systems, skid resistant surfaces and asphalt mixtures to provide packing density and flexural strength without affecting the chemical properties of binding system. Ground silica performs as functional extender to add durability, anti-corrosion and weathering properties in epoxy-based compounds, sealants and caulks [1][5][8][12].

2.2.4.7 Paint and coatings

Micron-sized industrial sands improve the appearance and durability of architectural and industrial paint and coatings. High purity silica contributes to brightness and reflectance, color consistency, and oil absorption. In architectural paints, silica fillers improve tint retention, durability, and design to dirt, mildew, cracking and weathering. Low oil absorption increases pigment loading resulted in improved finish color. In marine and maintenance coatings, durability of silica provides excellent abrasion and corrosion resistance [5][8].

2.2.4.8 Ceramic and refractories

Ground silica is an essential component of glaze and body formulations for all types of ceramic products. Low iron silica sand, some are calcined (heat treated) to convert quartz to cristobalite (high temperature form of silica), are ingredients of clay-based white ware ceramic bodies such as tableware, ornaments, sanitary ware, floor and wall tile as well as high tech ceramic which contains silica flour grounded to fine size to form major constituent of ceramic glazes [7][12]. Ground silica is used to decrease the viscosity and expansion coefficient in ceramic glazes as well as other ceramic applications. A typical glaze composition consists of 25% quartz or silica content [8].

In ceramic body, silica is a skeletal structure on which clays and flux components attach. SiO_2 is used to modify properties such as thermal expansion, regulate drying and shrinkage, and improve structural integrity as well as appearance. Silica products are also the primary aggregate in both shape and monolithic type refractories by providing high temperature resistance to acidic attack in industrial furnaces [5]. Crystalline silica is also the main component in production of ladle linings, refractory bricks and fluxes [1].

Advanced ceramic, like silicon nitride and silicon carbide represent a growing market for silica and silica based chemicals. Silicon carbide is manufactured by cooking silica sand or crushed quartz and oil coke at 2400°C in electric furnace for several days, with sawdust or rice husks are added to increase its porosity. Silicon carbide's thermal conductivity and expansion coefficient make it useful in refractory industry. Its applications include wear parts (slide bearings, seal rings, shafts and dynamic pressure) or composite bearings used in variety of pumps. Primary markets for silicon nitride are hybrid bearings, used in machine tool spindles, dental drills, aerospace components, vacuum systems and gyroscopes as well as engine components and cutting tools [8].

2.2.4.9 Filtration and water production

Industrial sand is used in the filtration of drinking water, processing of wastewater and production of water from wells. Its uniform grain shapes and grain size distribution characteristics provide an efficient filtration bed operation to remove contaminants in potable water and wastewater. Chemically inert, silica will not degrade or react when it comes in contact with acids, volatile organics, contaminants or solvents. Silica gravel is used as packing material in deep-water wells to increase yield from aquifer by expanding permeable zone around wall screen and preventing infiltration of fine particles [5][8][12]. Closely size silica sand is the main principal filtration medium used by water industry to extract solid from wastewater [1]. Silica sand preferred for water filters industry has a coarser particle sizes (0.5 to 1.0 mm) [7].

2.2.4.10 Oil and gas recovery

Known as proppant, or "fac sand", industrial sand is pumped down into holes in deep well application to prop open rock fissures and increase the flow rate of natural gas and oil. Silica's hardness and structural integrity combine together to deliver the required crush resistance to high pressure in wells up to 2450 meters deep. Its chemical purity resists chemical attack in corrosive environments [5]. Silica sand that has coarse size and spherical particles properties is being used in hydraulic fracturing to increase rock permeability for oil and gas recovery. The silica sand is pumped down oil wells and into oil-bearing strata to improve permeability and flow of oil into the well [1][7][8][12].

2.2.4.11 Recreational

Silica sand is used for golf course bunkers and greens as well as in construction of natural or synthetic athletic fields. In golf and sports turf, silica sand is the structural component of inert, uncontaminated and growing media. Silica sand is being used to repair greens and facilitate everyday maintenance such as root aeration, drainage media and fertilization. Natural grain shape and controlled particle size distribution of silica sand provides permeability and compaction properties for drainage, healthy plant growth and stability [5][7], [8]. Silica sand is also being used for equestrian surfaces, including weather horse racing tracks [1].

2.2.4.12 Plastics, polymer compounds, rubber, sealants and adhesives

Silica is also being used in plastics as extender, filler and reinforce. Whole-grain and ground silica are used for filler-type applications to thicken liquid systems, preventing plateout in polyvinyl chloride, as thixotropic and flatting agent. Silica flour provides resistance against abrasive actions and chemical attack. Self-cleaning exterior wall coatings and heavy duty offshore or marine paints are the typical examples. Intrinsic properties of silica flour promote its use in plastics for encapsulating electronic components application [1][7][8][12].

2.2.4.13 Agriculture

In agriculture, silica is used in farming, market gardening, horticulture and forestry such as conditioner or carrier for fertilizer and animal feed additives [1].

2.3 Nanomaterials

Nanotechnology is a new technology that is being integrated in many applications like telecommunications, electronics and biomedicine. Manipulation and producing materials at nanoscale or atomic and molecular level can change its chemical reactions, electricity, temperature, and magnetism [13][14]. Nanomodification can also improve a material's strength, shrinkage, ductility and impact resistance [13]. Nanotechnology is defined as an understanding and control of matter as well as dealing with particles having dimension between 1 and 100nm [13][16].

Nanomaterials are materials that have structural components with at least one dimension smaller than 100 nm with the potential to be as small as atomic and molecular length scales (~0.2nm) [15][17]. Nanomaterials are also generally known as nanoparticles, nanocrystals, nanocrystallites, sub-micron particles, 0D materials and colloidal quantum dots [18][19]. Nanoparticles can exist in amorphous or crystalline form. Their surfaces act as carriers for liquid droplets or gases. Examples of materials in crystalline form are fullerenes and carbon nanotubes, while traditional crystalline solid forms are graphite and diamond [17].

Depending on the method of preparation, nanoparticles, nanospheres or nanocapsules can be obtained [16]. Nanoparticles may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials [20].

2.3.1 Properties of Nanomaterials

Nanomaterials can have unique optical, magnetic, electronic or chemical properties [21][22]. Nanomaterials behave significantly different than bulk materials because of the surface effects which cause smooth properties scaling due to the fraction of atoms at the surface and quantum effects which show discontinuous behavior due to quantum confinement effects in materials with delocalized electrons. These factors affect chemical reactivity as well as mechanical, electric, optical and magnetic properties [17]. Nanomaterials have the potential to improve the properties of a material at a very small addition rate [15]. Fractions of atoms at the surface of nanomaterials increased because nanomaterials have a very large surface area and high particle number per mass. Small particle size contributes to more surface area per volume [15]. In catalytic industry, nanomaterials have proven to be good catalysts. Some nanomaterials also show bactericidal effects where surface to volume ratio is important [23].

Chemical reactivity increases with decreasing particle size due to the high specific surface area [17][24]. Binding energy per atom is lower with decreasing particle size. This results in melting point reduction with particle radius, following Gibbs-Thomson equation [17].

For physical properties, quantum effects lead to extraordinary material properties. While for biological, certain nanomaterials can penetrate cell membranes because of their small size. Since nanomaterials are so reactive, they tend to bond with each other and must be prevented with coatings if the nano-scale advantage is not to be lost [24]. Nanomaterials also exhibit improvements in permeability, strength, shrinkage, ductility and impact resistance [15]. Nanomaterials do have limitations. Their small size and large surface area lead to particle-particle aggregation, making physical handling of nanomaterials become difficult in liquid as well as in dry forms [16]. Nanomaterials are more reactive for geometrical reasons since proportion of surface atoms increases as the size of particle decreases. Surface atoms strongly inclined to make use of bonding possibilities [24].

Nanomaterials differ substantially from the properties of macroscopic solids in term of optical, magnetic, electrical as well as toughness, hardness and melting point. The general effects of decreasing particle size are [22]:

i. Higher catalytic activity (Pt or Al_2O_3)

ii. Higher mechanical reinforcement (carbon black in rubber)

iii. Higher electrical conductivity of ceramic (CeO_2)

iv. Lower electrical conductivity of metals (Cu, Ni, Fe, Co, Cu alloys)

v. Initially increasing and later decreasing magnetic coercivity, finally super magnetic behavior (Fe_2O_3)

vi. Higher hardness and strength for metals and alloys

vii. Higher ductility, hardness and formability of ceramics; lower sintering and super plastic forming temperature of ceramic (TiO_2)

viii. Higher blue-shift of optical spectra of quantum dots (quantum confinement of Si)

ix. Higher luminescence of semiconductors (Si, GaAs, ZnS: Mn^{2+})

2.3.2 Applications of Nanomaterials

Nano-sized particles below 10nm always attract great interest as the chemical and physical behavior from quantum size effect remarkably different from the bulk form. This give a huge potential for nanomaterials applications in electronic, chemical and mechanical industries, as well as in related technologies using catalyst, drug carriers, sensors, pigments, magnetic and electronic materials [25]. Usage of unagglomerated particles with sharp size distribution is preferred for practical applications and technologies especially for the purpose of compacting or self-arranging the particles [25]. Nanomaterials can be categorized into different areas of applications such as electronics, power and energy, health care and medical, engineering and environmental [19].

2.3.2.1 Electronic

Nanoparticles being utilized in electronic field to produce products such as displays, high density data storage, non-volatile RAMs, interconnections, EMI shields, small multilayer capacitors, optoelectronics devices as well as optical fibers joining and coating.

2.3.2.2 Power and energy

In power and energy field, nanoparticles are mainly used in solar cells, fuel cells, batteries, automotive catalyst and H_2 storage using metal hydrides.

2.3.2.3 Health care and medical

For health care and medical applications, nanoparticles are used for cancer treatments, virus detection, drug delivery, bone growth promoters, antioxidant drugs based on fullerences, anti-bacterial wound dressing, fungicide and inhalable insulin.

2.3.2.4 Engineering

Nanoparticles usage in engineering are for thermal barrier coatings, spark plug, chemical sensors, moisture barrier films for packaging, pigments and scratch resistant coatings, structural enhancement of polymers and coatings, inks-coducting and magnetic, cutting tool bits; consumer goods, anticounterfeit device, water or stain repellant textiles, adhesives for cardboard packaging, ski wax, antiglare or antimisting glass mirrors as well as tennis balls and rackets using nanoclays.

2.3.2.5 Environmental

Nanoparticles are also being used in environmental sector to produce environmental friendly antifouling paints and coatings, more sensitive sensors, alumina fibers for water treatment, self cleaning glass and pollution destroying paints [25].

2.3.2.6 Additive

Silica nanoparticles can be used as an additive for high performance and self compacting concrete that has improved workability and strength. Nanosilica proved to be an effective additive to polymers to improve its strength, flexibility and durability. Epoxy composites filled with functionalized nanosilica particles was obtained using sol-gel process. It was found that the modified particles could chemically bond to epoxy matrix, resulted in decrease in coefficient of thermal expansion (CTE) of the composites. The composites exhibit additional decrease in CTE with increased nanosilica content as well as an increase in glass transition temperature and decrease in damping. Cement mortars demonstrated an increase in its compressive and flexural strengths with the addition of nanoparticles. Strength of the mortars improved with increased nanosilica content, higher than when compared with addition of silica fume. SEM shows that nano-iron-oxide and nanosilica particles filled the pores and decrease the content of calcium hydroxide. These effects resulted in improvement of mechanical properties [26].

Well-dispersed nanoparticles increase the viscosity of the liquid phase, which helps to suspend cement grains and aggregates. This improves segregation resistance and workability of the system. Nanoparticles fill the voids between cement grains, which results in immobilization of free water (filler effect). Well-dispersed nanoparticles act as the centers of crystallization of cement hydrates, which accelerate the hydration. Nanoparticles favor the formation of small-sized crystals such as calcium hydroxide and AF_m. Nanosilica particles in pozzolanic reaction result in consumption of calcium hydroxide and formation of additional C-S-H. Nanoparticles improve the structure of aggregate contact zone, results in better bond between aggregates and cement paste. Crack arrest and interlocking effects between the slip planes provided by nanoparticles improve tensile strength, shear, toughness and flexural strength of cement-based materials [26].

2.3.2.7 Fillers

Composites of aluminium-based compounds and fumed silica particles are commonly used as fillers to improve the wear resistance of dental restorative materials [27].

2.3.2.8 Coating

The effect of coating on specific surface is nanoparticles fluidize as aggregates of several hundreds of micrometers in size. If the entire aggregates were coated, a drastic increase in specific surface area of nanopowders would occur. There is an expected change in surface area of coated nanoparticles as the thickness of film increases. This change occurs due to the slight increase in particle diameter as well as its effective density [27]. This allows it to have a wide range of applications such as in thermal barrier coating and electrolyte membrane for ceramic fuel cell [28].

2.3.2.9 Ceramic

Zirconia powder is a promising ceramic material because it possesses excellent strength, hardness, wear resistance and corrosion resistance [28].

2.3.2.10 Silica Gel

Silica gel is chemically inert non-toxic material composed of amorphous silicon dioxide. It has an internal network of interconnecting microscopic pores, yielding typical surface area of 700-800 square meters per gram. Water molecules absorbed or desorbed by these micro-capillaries until vapor pressure equilibrium is achieved with relative to the humidity of surrounding silica. Moisture absorbing properties of silica gels is affected by a few factors such as the capillary pore size or inclusion of hygroscopic salts, resulting in a wide range of performance. It is important to compare buffering capacity of different types of silica gels to determine which silica gel has the best performance for specific application [29].

The moisture buffering capacity of material is defined by its M value, which is the amount of water (in grams) that is gained or lost by 1 kilogram of silica gel for each 1% change in RH. M varies because of the following factors [29]:

i. Point along EMC/RH isotherm at which it is measured

ii. Magnitude of RH range used to determine M

iii. Whether it is measure along the adsorption or desorption isotherms (hysteresis) M_H

iv. Whether the hysteresis, M_H compensated M value was estimated or determined experimentally

2.4 Production of Nanoparticles

Techniques for the production of nanoparticles have been developed both in gas and liquid phase. The process needs to be low-cost and involves both continuous operation and high production rate to be industrially relevant [25]. There have been manifold attempts to create surface area by decreasing particle size of materials. Starting with bulk materials and making it smaller, breaking up larger particles by the use of physical process such as milling, crushing and grinding. Chemical methods of nanoparticles production is more familiar with small scaled materials starting from atomic scale by traditional wet phase chemical process and stopping the reactions at the right time to inhibit further particle growth, and thus the desired size is achieved [30].

2.4.1 Nanoparticles Production Methods

There are generally two approaches towards synthesis of nanosized materials [30]:

i. Bottom-up: material synthesis from atomic level

ii. Top-down: size reduction from bulk materials

Bottom-up techniques include laser, plasma, liquid phase or frame spray synthesis. These self-assembly preparation methods result in well controlled nanoparticles which are built on smaller building blocks allowing the synthesis of more complex materials or fabrication of nanoparticles with very narrow size distribution [30]. For synthesis of nanocomposites, different approaches have been developed such as incorporation of pre-made nanoparticles into polymer matrix with the use of common blending solvent or reduction of metal salt dispersed in polymeric matrix by the use of external reducing agent. Nanoparticles can be embedded in polymers using methods such as physical and chemical vapor deposition, ion-implantation and sol-gel synthesis routes [31]. The keys for nanoparticles preparation are [32]:

i. Formation of high-degree super saturation in narrow time or space

ii. Suppression of aggregation

iii. Monodisperse growth-Diffusion-controlled growth/Ostwald ripening

Classification of nanoparticles preparation methods can be done by two ways [28][32][33][34]:

i. In term of phase of medium for preparations (liquid phase/gas phase/vapor phase)

ii. In terms of the method of monomer preparation (physical/chemical)

2.4.2 Liquid-phase synthesis methods

The synthesis methods in the liquid-phase are coprecipitation, sol-gel processing, microemulsions, hydrothermal/solvothermal synthesis, microwave synthesis and sonochemical synthesis.

2.4.3 Gas-Phase Synthesis

Supersaturation is achieved by vaporizing material into a background gas, and then cooling the gas. Gas phase nanoparticles synthesis methods can be divided to the types of precursors being used [34]:

i. Methods using solid precursors
   - a. Inert gas condensation
   - b. Pulsed laser ablation
   - c. Spark discharge generation
   - d. Ion sputtering

ii. Methods using liquid or vapor precursors
   - a. Chemical vapor synthesis
   - b. Spray pyrolysis
   - c. Laser pyrolysis/photochemical synthesis
   - d. Thermal plasma synthesis
   - e. Flame synthesis
   - f. Flame spray pyrolysis
   - g. Low-temperature reactive synthesis

2.4.4 Vapor Phase Synthesis

Vapor phase synthesis has the same mechanism as liquid phase reaction. Vapor phase mixture rendered thermodynamically unstable relative to form the desired solid material. Once nucleation occurs, remaining supersaturation is relieved by condensation, or reaction of vapor phase molecules on resulting particles. This initiates particle growth phase. Rapid quenching after nucleation prevents particles growth by removing the source of supersaturation or slowing the kinetics. Coagulation rate is proportional to the square of number concentration (weak dependence on particle size). Nanoparticles in gas phase always agglomerate. Loosely agglomerated particles may be re-dispersed. Hard (partially sintered) agglomerated particles cannot be fully redispersed [34].

2.4.5 Top-down methods

Apart from bottom-up approaches mentioned above, top-down approaches such as milling has been known and applied. Modern milling technique like the ball milling generally straightforward and can yield nanoparticulate materials. However, there are a few drawback of this method such as low energy efficiency, necessity of liquid medium for nanoscaled material, susceptibility to impurities from abrasion and broader particle size distributions [30].

2.5 Ball Milling

Ball milling is a method for fine powder grinding and fabrication of sub-micron or nanostructured powder materials [36]. Ball mill is used for the purpose of grinding all kind of mines and materials [37][38]. Throughout the years, it has proved to be an effective and simple technique to produce nanocrystalline powders and the possibility of obtaining large quantity of materials [39].

Ball mill is the key equipment for grinding crushed materials. It has been widely used in the field of refractories, cement, advanced building materials, silicate product, chemical fertilizer, fire-pro of materials, glass, black and non-ferrous metal, ceramic and other mining department which can be used as anti-abrasion materials [37][38][40]. The possible minimum particle size for breakage using the ball milling method is in the range of 10 to 100nm, depending on the physical properties of material [41].

2.5.1 Types of Ball Milling

There are different types of ball milling methods which are categorized based on the movement of milling balls and jar, such as vibration mill, planetary mill and attritor [36]. Classification of ball milling is also made according to the grinding method; either wet grinding or dry grinding.

2.5.1.1 Vibration Mill

In general the vibrating mill consists of two parallel grinding cylinders which are fastened to the webs by clamps and anti-fatigue screws. This body builds the so-called swinging unit. At both ends of the grinding cylinders, inlet and outlet caps are flanged. Unbalanced masses are placed in the centre line of the webs in cylindrical roller bearings to create the effect of circular movements of the grinding cylinders. At the height of the centre line, the shaft with bearings as well as the adjustable unbalances masses are connected with cardan and coupled to an electric motor. The swinging body is being supported with lugs on special elements attached to the machine frame [42].

The vibrating mill belongs to the group of mills that utilize the impact forces. However, in contrast to the so-called impact mill, the size reduction in vibrating mills is primarily caused by the impact energy of the grinding media rather than by friction or by acceleration of the feed material. Usually rotation impulses of 1000 min^{-1} are transferred by the effect of unbalanced weights from the surface of the grinding cylinders to the grinding media, which performs an almost ideal circular movement. Depending on the frequency and unbalanced mass, an acceleration of several g can be generated (g=acceleration of gravity). The grinding effect is caused by milling the feed material in between the elements of the grinding media and between the elements of the grinding media and the cylinder walls [42].

In addition to the grinding effect based on impact energy, a minor degree of friction forces are generated between the walls and the grinding media, which also leads to a certain size reduction of the feed material. Friction resulted from the rotation energy of each grinding bed against the rotation direction of the unbalanced masses. However, the milling effect is primarily caused by impact and to a minor degree of friction only. Furthermore, a rotation of the entire grinding bed is generated due to the circular movement. Gravity is the driving force of the grinding media [42].

2.5.1.2 Planetary mill

The planetary ball mill owes its name to its planet-like movement of the jars. These jars are arranged on a rotating support disk and a special drive mechanism causes them to rotate around their own axes. The centrifugal force produced by the jars rotating around their own axes and that produced by the rotating support disk both act on the jar contents, containing the material to be ground and grinding balls. Since the jars and the supporting disk rotate in opposite directions, the centrifugal forces alternately act in like and opposite directions. This causes the grinding balls to run down the inside wall of the jar, known as the friction effect, followed by the material being grounded and grinding balls lifting off and traveling freely through the inner chamber of the jar and colliding against the opposing inside wall, a phenomenon known as the impact effect [43].

Even though the disk and the jar rotation speeds could not be independently controlled in the earlier versions of planetary mill, it is possible to do so in the modern versions. In a single mill, one can have either two or four milling stations. Recently, a single station mill was also developed. Grinding jars and balls are available in eight different materials. They are agate, silicon nitride, sintered corundum, zirconia, chrome steel, Cr-Ni steel, tungsten carbide and plastic polyamide [43].

(a) Planetary Ball Mill Technology

The grinding jars are arranged eccentrically on sun wheel of planetary ball mill. Grinding balls in grinding jars are subjected to superimposed rotational movements, known as the Coriolis forces. The difference in speed between grinding balls and grinding jars produces interaction between frictional and impact forces, releasing high dynamic energies. The interplay between these forces produces high and very effective degree of size reduction of planetary ball mill [44].

(b) Speed Ratios

The working principle of planetary ball mill is based on relative rotational movement between grinding jar and the sun wheel. Other than sun wheel diameter and speed of rotation, this speed ratio is decisive of energy input and therefore for the results of size reduction process. The higher the speed ratio, the more energy is generated. Planetary ball mills have different speed ratio settings. The direction of movement of the sun wheel is opposite to that of grinding jars in the ratio of 1:-2 or 1:-2.5 or 1:-3. A ratio of 1:-1 means each time sun wheel rotates, grinding jar also rotates exactly once in different direction (indicated by minus sign). With speed ratio 1:-2, grinding jar rotates twice for each sun wheel rotation [44].

2.5.1.3 Attritor mill

An attritor is a ball mill that is capable of generating higher energies. An attritor consists of a vertical drum with a series of impellers inside it. The drum is set progressively at right angles to each other. The impellers energize the ball charge, causing powder size reduction due to the impact between balls, between balls and jar wall as well as between wall, agitator shaft and impellers. Some size reduction appears to be done by interparticle collisions and by ball sliding. A powerful motor rotates the impellers, which in turn agitate the steel balls in the drum [43].

By using attritor mill, large quantities of powder, ranging from about 0.5 to 40 kg can be milled at a time. The grinding tanks or jars are available in stainless steel or stainless coated inside with silicon carbide, alumina, zirconia, silicon nitride, rubber and polyurethane. A variety of grinding media is also available such as glass, steatite ceramic, flint stones, silicon carbide, mullite, sialon, silicon nitride, zirconium silicate, alumina, stainless steel, zirconia, carbon steel, chrome steel and tungsten carbide [43].

The operation of an attritor is simple. The powder to be milled is placed in a stationary tank together with the grinding media. The mixture is then agitated by a shaft with arms, rotating at a high speed of about 250 rpm. This causes the media to exert both shearing and impact forces on the material to be grinded. The laboratory attritor can works up to 10 times faster compared to the conventional ball mills [43].

2.5.1.4 Wet Grinding

The void volume between the grinding media with mill half charged represents 20% of total volume of mill, and with one-third charge of grinding media 13½ %. The fastest grinding occurs where there is sufficient material in batch to fill all voids and slightly covers grinding media. This equals approximately 25% of total volume with half ball charge and 18% with one-third ball charge. The material should never be allowed to drop below the surface of grinding media, because excessive wear can occurs to the mill and grinding media as well as contaminating the material. The largest batch should not exceed 60% of total mill volume [45].

(a) Consistency or Viscosity of Material

The most important element in wet grinding is the consistency or viscosity of batch. Low viscosity materials allow grinding media to move with an excessive speed and this combined with the thin protective film around media may cause abnormal wear, contamination and heat build-up. If low viscosities cannot be avoided, then it is recommended that small grinding media is being used.

Based on the accepted milling techniques, following consistencies measured at milling temperature are usually works out best [45]:

i. For flint pebbles and porcelain balls 75 to 90 Krebs Units, 600 to 1100 centipoises

ii. For high density balls 90 to 100 Krebs Units, 1100 to 2100 centipoises

iii. For steel balls 90 to 115 Krebs Units, 1100 to 2400 centipoises

(b) Wetting Agents

The use of wetting agents can greatly increased the capacity of ball mills and pebble mills without altering the viscosity during the grinding process. In the case of one operator who is prior to use wetting agents, he could load no more than 50% solids to retain suitable working viscosity. However, by adding proper wetting agent, he was able to increase the solids content up to 85%. Combined with increased production, grinding operation can be performed in a much faster time since wetting agents break down surface tension of aggregated particles and finished product has greater stability [45].

It is sometimes highly advisable to add sufficient additional liquid to thin down the batch. If the mill is equipped with discharge valve, then the liquid is best being added into batch through the valve. There is likely to be some underground materials that are packed between flanges of manhole frame and cover. To prevent from dropping this material into the finished batch, it is advisable to avoid disturbing the cover until ground material has been removed [45].

2.5.1.5 Dry Grinding

Production using milling method is sometimes being done dry to avoid separate drying step. Dry grinding also can avoid formation of hard agglomerates as there is no liquid present. Dry grinded ceramic is usually used in the pressing operations to make a shape and to consolidate the particles. Crushing and milling are two sequential processes for particle size reduction. Crushing helps to reduce particle size of hard materials until about 80 mesh measured using the Tyler Sieves. After achieving this size reduction, other finer reduction techniques can be used. There are two types of crushers that are the most commonly used, the jaw crushers and roll crushers [46].

Usually dry grinding is done in a ball mill with milling media. Portland cement is dry milled commercially by using steel balls for efficiency. An Alumina media of about three inches in diameter is used for milling the white cement. Hard ferrites are also being dry milled in air swept ball mills. Bayer aluminas are another example of dry milling product. In lab, dry grinding is not common since the cost of drying is a constraint. However, when the product, which is originally wet milled in the lab being transferred to the production where it is dry milled, properties of powders will be different and this will cause start-up problems. Dry grinding is not effective in small diameter mills as it lacks enough energy to fracture and crush the particles. Mills with about a 12-inch diameter are more suitable. Higher energy mills such as planetary and stirred mills are also available.

A serious problem with dry grinding is the powder will cake onto the sides of the mill and prevent them from receiving further size reduction. Scraping the mill down periodically will help to reduce the caking problem. Another way to reduce caking problem is to add a surface active agent. It is believed that Bayer alumina dry milling involves the usage of ethylene glycol. Bone-dry powders have less caking tendency compared to the powder that is exposed to humidity. Powders can also be dried and immediately put into the mill while the powders are still hot [46].

2.5.2 Ball Milling Mechanism

Ball mill is made up of feeding part, gyre part, discharging part, transmission part such as decelerator, small transmission gear, generator, electrical control and so on. Hollow axis adopts the cast steel and rotary big gear is processed from cast rolling gear [40].

Ball mill is a horizontal rotating device which is transmitted by an outer gear. Material transferred to the grinding chamber through quill shaft uniformly. There are ladder liner and ripple inner as well as different specifications of steel balls in the chamber. Centrifugal force caused rotation of the barrel brings steel balls to a certain height, producing the impact and grind the materials. Ground materials are discharged through the discharging board and thus the grinding process is completed [38].

To use the ball mill, materials to be ground are loaded into Neoprene barrel which contains the grinding media. As the barrel rotates, the materials are crushed between individual pieces of grinding media that mix and crush product into fine powder over a period of several hours. The longer ball mill runs, the smaller powder will be. Ultimate particle size depends on how hard the ground material is and how long the ball mill runs [40].

2.5.3 Advantages of Ball Milling

There are a number of advantages when using ball milling technique [37]:

i. Easy and safe operation

ii. Stable performance

iii. Even product size

iv. Low energy consumption

v. Low investment, high return

2.5.4 Ball Milling Parameters

Optimization of ball milling parameters is crucial for the efficiency of grain size and particle size reduction in the fabrication of nanostructured powder. Taguchi technique provides a simple, efficient and systematic approach to determine optimal parameters in manufacturing process. It is being used to study the entire parameters space with small number of experiments rather than testing all possible combinations. Statistical analysis of variance (ANOVA) can then be performed to identify statistically significant parameters [36].

The known main parameters of planetary ball milling are weight ratio of ball to powder, ball size, type of milling medium, volume of jar, milling time, and rotation speed. Larger volume of ball milling jar and higher rotation speed can improve grain size and particle size reduction at the same time [36][39]. Of all the main parameters, the ball to powder ratio and its diameter, milling time and rotation speed are recognized as the most crucial parameters [47].

2.5.4.1 Type of Mill

There are different types of mill that differ in capacity, operation speed and ability to control the operation by varying temperature of milling and extent of minimizing powders contamination. Depending on the type of powder, quantity of powder and final constitution required, a suitable mill can be chosen. Planetary ball mills or attritors are commonly used to produce milled powder in large quantities. There are specially designed mills that are used for specific applications [43].

2.5.4.2 Milling jar

Milling jar (grinding vessel, vial, container or bowl) material is important since there will be impact from grinding medium on inner walls of jar. Some material may get dislodged and incorporated into the powder. Contamination of the powder can happened or the powder chemistry being altered. If grinding vessel material is different from the powder, then the grinding vessel material may contaminate the powder. If the two materials are the same, alteration in the chemistry might happen unless proper precautions are taken to compensate additional amount of element incorporated into the powder. Hardened steel, hardened chromium steel, tempered steel, tool steel, stainless steel, WC-lined steel, WC-Co and bearing steel are the most common materials being used for grinding vessels. Some specialized purposes require specific materials such as titanium, copper, sintered corundum, yttria-stabilized zirconia, sapphire, partially stabilized zirconia + yttria, hard porcelain, agate and Cu-Be. Shape of the jar especially the internal design also seems to be important. Alloying was found to occur more commonly in flat-ended jar at a significantly higher rate compared to round-ended jar [43].

2.5.4.3 Weight ratio of balls to powder

Weight of the balls to powder ratio (BPR) is also referred to as charge ratio (CR). The commonly used ratio is 10:1 for milling powder in small capacity mill. However, higher BPR of up to 50:1 or even 100:1 is also being used when conducted in large capacity mill such as attritor. BPR has a significant effect on the time required to achieve particular phase in the milled powder. Higher BPR will shorten the required time. At high BPR, since the weight proportion of the balls increases, number of collisions per unit time is also increases. Therefore, more energy is being transferred to powder particles and alloying takes place faster. Due to the high energy, more heat is generated and changes the powder constitution. Amorphous phase may even crystallize if the temperature rise is substantial [43].

The best level to be used is 15:1 for grain size reduction and 20:1 for the particle size reduction. So for a volume of milling jar, a weight ration of ball to powder higher than 15:1 can improve the reduction of particle size [36].

2.5.4.4 Milling balls size

Larger balls size provides higher energy in the rotation movement of the mill and impacts with higher energy between balls and ball milling jar, which will improve deformation and fracture of particle, so the reduction of grain size is also improved. Medium balls size can help to grind the particles, and also prevent cold welding and agglomeration. Smaller balls size provides lower impact energy. But very large balls size can cause serious cold welding and agglomeration, which will deteriorate the particle size reduction [36]. Stirred bead mill with very small beads can be used as efficient equipment for the production of colloidal particles in nanoscale from feed materials of several microns in size at high energy consumptions [41].

Theoretical basis of the grinding technology for stirred bead mills indicated that transmitted grinding energy is proportional to two key values; number of contacts per unit time between grinding beads and particles, and the intensity of the contacts. If the particles size of the product to be grounded decreases, compensation can be made with correspondingly smaller grinding beads, at the same time the intensity of impact of grinding beads decreases proportionally to their mass. Limited compensation can be made for this effect by using higher contact speeds. Fineness that can be achieved is also limited by impact energy required to fracture the particles and sufficiently high number of contacts, primarily dependent on grinding bead diameter [41].

The most common cause for faulty operation and complaints has been due to the size of grinding media. It is recommended that smallest feasible grinding media is being used. The optimum size of grinding media should not change with the mill size. If laboratory pebble or small ball can successfully grinds a sample batch in the lab mill, the same size grinding media will do the best job in production mill whether the mill is one foot or eight feet in diameter. Small grinding media is recommended because [45]:

i. It provides higher grinding contacts per revolution compared to larger media. This results in a much quicker grinding action

ii. It provides smaller voids, limiting the size of particles or agglomerates

iii. It does not create excessive energy which cannot be utilized. Oversized grinding media frequently developed more grinding energy than necessary. This excess energy builds up heat and wears down the media and lining, resulted in contamination of the batch.

However, small size of grinding media has a few disadvantages such as:

i. The discharging process takes longer time due to the increased surface tension in smaller voids

ii. Using extremely small media with greater surface area for material to adhere to may yield smaller initial batch. However, subsequent batches will be of normal size

2.5.4.5 Types of milling medium

The best medium for grain size reduction is ethanol but for particle size reduction the best medium is distilled water. Surface tension of ethanol in air is similar to that of acetone and 75% ethanol water solution, but it is far less than that of distilled water. Researchers reported that the surface tension of the milling medium could enhance milling efficiency. There are two mechanisms for the effect of surfactant in ball milling. The first is the surfactant absorbed on surface of brittle materials can reduce the hardness of brittle materials. Secondly, a surfactant can reduce the viscosity of slurry of the powder mixture [36].

2.5.4.6 Volume of ball milling jar

Larger volume of jar can improve both the grain size and particle size. Ideal status of the mixture (powder and medium) in the jar is the slurry. The powder can be absorbed on the surface of the balls as well as the jar. Slurry of powder mixture can improves heat transferred from frictions. With increasing ball milling temperature, volume of liquid in slurry decreases, or even disappears for jar with low evaporation point. So, by increasing the volume of jar, slurry of the mixture can be keep within certain viscosity which can improves ball milling effect [36].

2.5.4.7 Percentage of jar filling

Since alloying among powder particles occurs due to the impact forces exerted, there should be enough space for the balls and powder particles to move around freely inside the milling jar. Percentage of jar filling with the powder and balls is important. If quantity of the balls is very small, the production rate will be very small. If the quantity is large, there will be no enough space for the balls to move around and will resulted in less impact energy. Generally, about 50% of jar space is being left empty so that the jar is not overfilled [43]. For the most efficient results, the mill should be at least half filled with the grinding media [45].

2.5.4.8 Milling atmosphere

Powder contamination is the major effect of milling atmosphere. Therefore, powders are milled in jars that have been evacuated or filled with inert gas such as helium or argon. High purity argon is the most common ambient to prevent oxidation and powder contamination. The presence of nitrogen ambient can be prevented or minimized by oxidation. Different atmospheres are used for specific milling purposes. Nitrogen or ammonia atmosphere are being used to produce nitrides. Hydrogen atmosphere is used to produce hydrides. Presence of air in jar will produce oxides and nitrides in the powder, especially if the powders are reactive in nature. The types of atmosphere are also observed to affect the final phase nature. When Cr-Fe powder mixtures were milled in argon atmosphere, no amorphous phase was formed. However, when the powder was milled in air containing argon or nitrogen, the powder became completely amorphous. Oxygen was similarly shown to enhance amorphization kinetics in Ni-Nb system [43].

2.5.4.9 Process control agents

Cold welding among particles will happened especially if the particles are ductile due to the heavy plastic deformation experienced during milling. Only when there is a balance between cold welding and particles fracturing that the true powder particles alloying can occur. A process control agent (PCA), also referred to as surfactant or lubricant is added to powder during milling to reduce cold welding effect. PCAs can be liquids, solids or gases and act as a surface active agent. PCA absorbs on powders particles surface and minimizes cold welding between powder particles and inhibits agglomeration. The surface-active agents interfere with the cold welding and lower surface tension of solid materials.

A wide range of PCAs has been used at a level of about 1-5 wt% of total powder charge. Among the PCAs that are commonly used comprise of hexane, methanol, stearic acid and ethanol. PCAs affect the final phase formation, modifying glass-forming range, changing solid solubility levels and altering contamination levels. The presence or air in milling jar or milling of powders at very low temperatures (cryomilling) has shown to minimize welding due to the increased brittleness of powder particles at low temperatures. Metal powders (with fcc structure) that are being milled in hydrogen atmosphere have been found to become brittle and not sticking among themselves or the jar due to the hydride phase formation.

Nature and quantity of PCAs being used and the type of powder being milled would determine the final size, shape and purity of powder particles. Larger quantity of PCA reduces particle size by 2 to 3 orders of magnitude. Increase of PCA content leads to exponential decrease of powder size. However, the use of PCA is not required when milling brittle materials as no large particles will be observed. Homogeneous particle size distribution can be easily achieved when PCA is in liquid state (e.g., ethyl acetate) than in solid state (e.g., stearic acid) [43].

2.5.4.10 Milling speed

Depending on the mill design, there are limitations to maximum speed that can be employed. In conventional ball mill, increasing rotation speed will increase the speed with which the balls move. Above critical speed, the balls will be pinned to the jar inner walls and will not fall down to exert impact force. Therefore, maximum speed should be just below the critical value so that the balls fall will down from maximum height to produce maximum collision energy.

Another maximum speed limitation is when at high speeds or intensity of milling, jar temperature may reach high value. In some cases that require diffusion to promote homogenization and alloying in powders, this may be advantageous. But in some cases, temperature increase is a disadvantage since this will accelerates transformation process and results in supersaturated solid solutions decomposition or other metastable phases formed. Contamination of powder may also be generated from high temperatures. The smaller the mill, the faster in RPM it must run to attain critical speed. The rule of speed applies regardless of the type of grinding media [45].

2.5.4.11 Milling time

The time required varies depending on the ball to powder ratio, intensity of milling, type of mill and milling temperature. For each parameters combination and particular powder system, the milling time has to be decided. However, it should be realized that contamination level increases and some undesirable phases will form if powder is milled for times longer than required. The powder should be milled just for the required duration and not any longer [43].

2.5.4.12 Temperature of milling

The alteration of milling temperature was done either by dripping liquid nitrogen into milling jar to lower the temperature or electrically heating milling jar to increase the temperature. It was reported that at higher temperature, root mean square (rms) strain in the material was lower and has larger grain size. Solid solubility extent decreases at higher temperature. Higher milling temperature was also observed to enhance amorphization kinetics [43].

2.5.4.13 Grinding balls

Tool steel, chromium steel, tempered steel, stainless steel, hardened steel, WC-Co and bearing steel are the most common types of grinding balls materials. For the ball to create enough impact force on the powder, density of grinding balls should be high enough. The grinding balls size also has an influence on the milling efficiency. Grinding balls with large size and high density is useful since larger balls weight will transfer more impact energy to powder particles. Size of the grinding jar used has been reported to influence the final constitution of powder. Smaller balls produce intense frictional force, promoting formation of amorphous phase. Soft milling conditions (small ball sizes, lower ball to powder ratios and lower energies) favor the amorphization or metastable phase formation.

It has been predicted that if balls with different diameters are being used, highest collision energy can be obtained. In the initial stages of milling, the powder gets cold welded and also coated onto the grinding jar surface. This is advantageous since it avoids contamination of powder due to the grinding jar wear. However, to avoid formation of heterogeneous final product, this layer thickness must be kept to minimum. But the disadvantage will be low powder yield and it is difficult to detach the powder. To minimize amount of powder coated onto the balls surface and cold welding, combination of large and small size balls can be used. Different balls size produce shearing stress that helps to detach powder from balls surface. It is also necessary to use several sizes of balls to randomize balls motion to avoid a well-defined trajectory [43]. There are a few types of grinding balls that are most commonly used; flint pebbles, porcelain balls, high density media, steel and other metal balls [45].

(a) Flint Pebble

Flint pebble is the oldest type of grinding media being used and still continues to be extremely popular. They can be used with all types of lining. Among the industries in which they are used include paint and enamel products, ceramic slip and glaze, latex compounds, aniline dyes, graphite and clay mixtures for lead pencils and hundreds of other products requiring the finest results without contamination. They are exceptionally tough and longwearing and can last many years regardless of the kind of service [45].

(b) Porcelain Balls

Porcelain balls are pure white ceramic material with dense and highly vitrified body that will not chip or crack in service. They have been immensely improved in quality throughout recent years and are being used exclusively in many industries [45].

(c) High density media

High density media is the latest grinding media developed for ball and pebble mills. It is made with high alumina oxide content and has a density of 40 to 50% greater than regular porcelain balls. They are also being fired at higher temperature, making them harder and more abrasion resistant [45].

(d) Steel and other metal balls

Steel balls are unquestionably doing faster grinding job than any other commercially available media. They have been proven to be effective especially in the paint industry. The following types of metal balls are commonly used in ball mills [45]:

i. High Carbon – high manganese steel with alloying elements or molybdenum, chromium or nickel. These balls uniformly hardened until 60 to 65 Rockwell C. They represent highest quality of all metal balls and most operators insist on using them

ii. Cast Nickel Alloy – this is also a very popular grinding ball. As it is basically white metal ball, it causes less metallic staining compared to the others. Principal objection is its rough outer surface and projecting nubs typical of cast balls. It requires long conditioning periods before can be placed into general use.

iii. Stainless Steel – because of their high cost they are only being used on special work requiring an acid resistant and non-magnetic ball

iv. Chilled Iron

v. Forged Low Carbon Steel – both 4 and 5 are the cheapest metal balls obtainable. They are only recommended for rough grinding, where metallic contamination is not objectionable

vi. Other, more special types include bronze or brass, aluminium and tungsten carbide

2.6 Production of nanoparticles by ball milling

There are a lot of researches that used ball milling as a method to produce nanoparticles. The summary of previous works on nanoparticles production by ball milling can be viewed in Table 2-1.

Table 2-1 Nanoparticles production by ball milling from previous works

Author	Materials	Type of ball mill	Time of milling	Particle size
Guoxian *et al.* [48]	Nanostructured tungsten carbide/cobalt powder (WC-Co)	Planetary ball mill	10 hours	400 nm
Kalala *et al.* [49]	Carbonate and silica nanoparticles	Stirred bead mill	4 hours	50 nm
Monov *et al.* [50]	ZnO nanocrystalline	Planetary ball mill	5 hours	10-25 nm
Ramezani *et al.* [51]	Hydroxyapatite	Planetary ball mill	2 hours	40-60 nm
Abdellaoui *et al.* [52]	Aluminium zirconium powder	High energy planetary ball mill	24 hours	-
Asano *et al.* [53]	Mg-Ti alloys	Planetary ball mill	50-200 hours	-
Puszkiel *et al.* [54]	MgFe material	Low energy mill and high energy mill	-	20-30 nm
Xu *et al.* [55]	ZnO varistor	High energy planetary ball mill	5 hours	-
Fang *et al.* [56]	Ti-50%Al composite powder	High energy planetary ball mill	9 hours	-
Liang *et al.* [57]	Expanded graphite	High-energy planetary ball mill	100 hours	-
Tian *et al.* [58]	Maize starch granule	Planetary ball mill	2 hours	-
Chen *et al.* [59]	Fe_3SO_4 nanoparticles	Planetary ball mill	100 hours	30-80 nm
Leyang, D., *et al.* [60]	Nano-Fe powder	-	10 hours	100 nm
Yadav *et al.* [61]	Titania (TiO_2)	High-enery attritor ball mill	10 hours	10-20 nm
Zakeri *et al.* [62]	Al_2O_3-TiC nanocomposite powder	Planetary ball mill	35 hours	7 nm
Anjumn *et al.*	PLGA polymer	Planetary micromill	1 hour	-

[63]				
Akhila *et al.* [64]	Nimesulide and polymer	-	-	165 nm
Bilgili *et al.* [65]	Pigment nanoparticles	Stirred media mill	24 hours	10-100 nm
Chen *et al.* [66]	Carbon nanotubes, BN nanutubes, Zn nanowires, SiC nanowires	Vertical rotating ball mill and planetary ball mill	50 hours	-
Akash *et al.* [67]	Ultrafine Halide Crystallites	Pulverisette ball mill	8 hours	-
Chen *et al.* [68]	Magnesium ferrite $MgFe_2O_4$ nanoparticles	Planetary ball mill	60 hours	30 nm
Kong *et al.* [69]	Ultrafine $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramics	Planetary high energy ball mill	20 hours	10 nm
Zhang *et al.* [70]		Planetary ball mill	4 hours	60 nm
Kani *et al.* [71]	Zeolite HY	Attritor mill	2 hours	70 nm
Hedayati *et al.* [72]	Poly (ether ether ketone)/surface modified silica nanocomposite	Planetary high energy ball mill	15 hours	-
Xueqing *et al.* [73]	Expanded graphite-Fe mixture	Planetary high energy ball mill	100 hours	-
Avolio *et al.* [74]	Cellulose	Planetary ball mill	1 hour	120 nm
Avettand *et al.* [75]	W-Y powders	Planetary ball mill	72 hours	-
Hewitt *et al.* [76]	Nanostructured WC-Co composites	High energy horizontal ball mill	5 hours	21 nm
Zhang *et al.* [77]	Nb-W-Mo-Zr alloy powder	High energy ball mill	60 hours	14 nm
Yadav *et al.* [78]	Nanocrystalline cerium oxide	High-energy attritor ball mill	30 hours	10 nm
Liu *et al.* [79]	TiF_3-doped $LiAlH_4$	Planetary ball mill	18 hours	43 nm
Rud *et al.* [80]	Mg-C powder mixture	Planetary ball mill	-	-

Planetary ball mill is preferred compared to other types of mill such as attritor mill or stir bead mill. The high and very effective degree of size reduction as a result of high dynamic energy produced when using planetary ball mill makes it a finer choice [81]. The milling time for each works highly varies from one another, ranging from 1 hour up to until 200 hours. This may be resulted from different parameters used which will determine the effectiveness of the milling or the properties of the material to be milled. Materials with higher hardness will take longer time for the size to be reduced to nanosized region.

2.6.1 Experimental details from previous works

Table 2-2 and Table 2-3 provide the summary of experimental details of previous works in nanoparticles production by ball milling. Information such as ball to powder weight ratio, rotation speed and milling atmosphere give further understanding and comparison of previous works.

Table 2-2 Experimental details of previous works on nanoparticles production by ball milling

Ref.	**Parameters**			
	BPR	**Grinding balls material**	**Rotation speed**	**Milling atmosphere**
Guoxian *et al.* [48]	15:1 for grain size reduction 20:1 for particle size reduction	WC-10wt% Co hardmetal	-	Pure argon
Kalala *et al.* [49]	-	Yttrium-stabilized zirconia	-	-
Monov *et al.* [50]	20:1	Zirconia	350-400 rpm	-
Ramezani *et al.* [51]	10:1	Stainless steel, agate	400 rpm	-
Abdellaoui *et al.* [52]	17:1	Stainless steel	360 rpm	Argon
Asano *et al.* [53]	-	Zirconia	200 rpm	-

Puszkiel *et al.* [54]	-	-	-	Argon
Xu *et al.* [55]	20:1	Zirconia	100 rpm	-
Fang *et al.* [56]	-	-	400 rpm	Argon
Liang *et al.* [57]	40:1	Steel	450 rpm	-
Tian *et al.* [58]	-	-	500 rpm	-
Chen *et al.* [59]	50:1	Iron	300 rpm	-
Yadav *et al.* [61]	40:1	Stainless steel	400 rpm	-
Zakeri *et al.* [62]	10:1	Stainless steel	500 rpm	Argon
Anjumn *et al.* [63]	-	Agate	200 rpm	-
Akhila *et al.* [64]	-	Iron	84 rpm	-
Bilgili *et al.* [65]	-	Crosslinked polystyrene	2000 rpm	-
Chen *et al.* [66]	-	Hardened steel	300 rpm	N_2, NH_3, gas
Akash *et al.* [67]	20:1	Tungsten carbide (WC)	-	-
Chen *et al.* [68]	100:1	-	200-400 rpm	-
Kong *et al.* [69]	20:1	Tungsten carbide	200 rpm	-
Zhang *et al.* [70]	10:3	Zirconia	400 rpm	Argon
Kani *et al.* [71]	-	-	600 rpm	-
Hedayati *et al.* [72]	26:1	Hardened Cr steel	280 rpm	Argon
Xueqing *et al.* [73]	40:1	Steel	450 rpm	-
Avolio *et al.* [74]	10:1	Steel	-	-
Avettand *et al.* [75]	16:1	WC-Co	400 rpm	Argon

Hewitt *et al.* [76]	10:1	Cr_6	-	Argon
Zhang *et al.* [77]	20:1	WC hard metal	450 rpm	Argon
Yadav *et al.* [78]	40:1	-	400 rpm	-
Liu *et al.* [79]	-	Steel	300 rpm	Argon
Rud *et al.* [80]	30:1	Steel	400 rpm	Argon

The ball to powder weight ratio used by previous works clearly varies from one another. Although majority of the ratio used were in the range of 10:1 to 20:1, there are works that have used ratio much higher than that, going up to 100:1. Higher ball to powder weight ratio helps to increase the particle size reduction rate. However when the ratio used is too high, there is a possibility that contamination from the grinding balls and inner wall of milling vial will happened. The balls sizes used for nanoparticle production are mostly 10 mm and smaller.

From Table 2-2, it is clear that almost all of previous works preferred wet grinding rather than dry grinding. Ethanol and distilled water are usually used by the researchers opted for wet grinding method. Stearic acid is also being used as process control agent to avoid the agglomeration problem. According to Zhang [70], ethanol is the best milling medium for grain size reduction while distilled water is the best medium for particle size reduction. Wet grinding however will require separate drying process and the possibility of forming hard agglomerates if no chemical or process control agent is used.

Most of the nanoparticles produced by ball milling are also performed in glove box under Argon gas temperature. The use of Argon gas temperature is for the purpose of minimizing and avoiding contamination to the samples. The material of grinding balls and milling vial used will influence the contamination level of the samples. Balls and vial of the same material as the sample to be grinded are advised as this will reduce and avoid contamination from collisions between balls as well as between balls and inner wall of vial. Hard material such as zirconia and stainless steel which are widely chosen from previous works can be used as this will reduce the possibility of contamination during milling.

Apart from the parameter mentioned above, another parameter that has high influence on milling effectiveness is the milling speed. Almost all of the researches used high rotation or milling speed, which is more than 100 rpm. In fact, a milling speed as high as 2000 rpm was used as has been demonstrated by Bilgili [65]. Higher milling speed provides higher impact energy exerted by the grinding balls onto the materials and resulted in better milling effectiveness.

2.7 Chapter Summary

This chapter has showed the relevant literature reviews regarding the topic of nanoparticles, silica sand and ball milling. The literature reviews provide a fundamental understanding of the overall scope in this research. It also explained the unique characteristics and applications of silica sand as well as nanoparticles, hence revealing the significance of this research. Previous works on nanoparticles production using ball milling have also been discussed. The detailed explanations on the previous experimental works especially the parameters used have been compared and analyzed as guidance for the experimental works in this research.

CHAPTER III

METHODOLOGY

3.1 Chapter Overview

This chapter presents the methodology used in the research. Sample preparation which involves sample deposits and pre-milling processes are explained. This chapter also discussed the equipments used, processes involved and the parameters investigated. Analysis methods and equipments used are also included in this chapter.

3.2 Research Procedures

The research started with identifying suitable location for silica sand deposits. The location of silica sand deposits is fixed as silica sand from multiple sources might contain different composition. The natural silica sand is then washed and any impurities of contaminants are removed. The washed silica sand is dried in oven to eliminate moisture from the sample. After the drying process, the silica sand is sieved to get a uniform starting size for all experiments that are going to be done. A series of experiments designed using Taguchi method are performed and the results are analyzed using Signal-to-noise ratio (SN ratio) and ANOVA method calculations to determine the optimum parameters. Using the optimum parameters, a lab-scale production is done to test the ability of producing silica sand nanoparticles consistently. The production time is observed to study the minimum time required for silica sand nanoparticles production. The results from lab-scale production are analyzed using particle size analyzer, Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray analysis. The process flow chart of research procedures is shown in Figure 3-1.

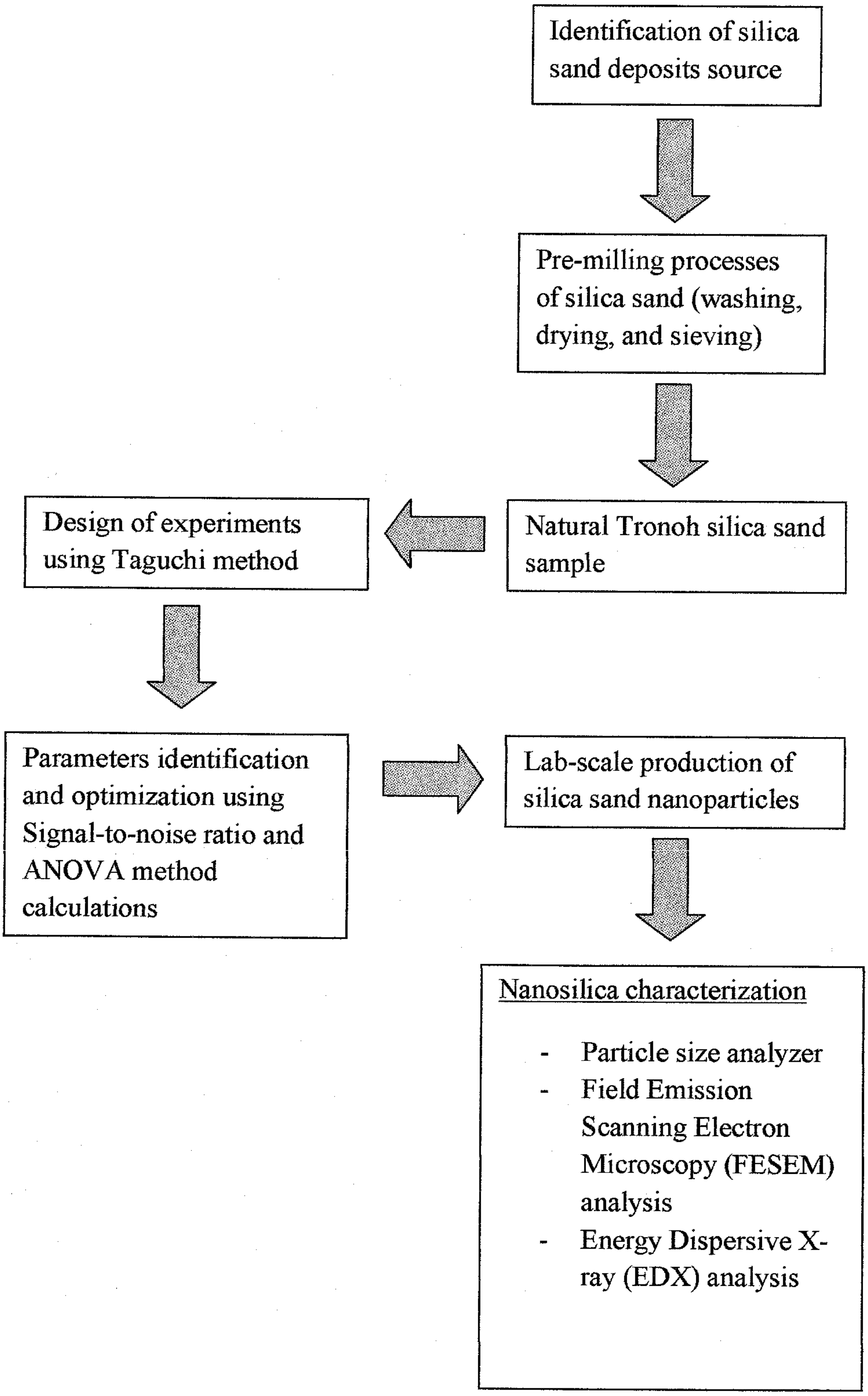


Figure 3-1 Flow chart of research methodology

3.3 Silica Sand deposit

The location of silica sand deposit has been carefully chosen to be far from construction areas. This is done to avoid mixture between natural silica sand and construction sand. The silica sand deposit is an abandoned mining site located 3 km from Universiti Teknologi Petronas and 1.5 km from Tronoh town. Figure 3-2 shows the satellite map image of the silica sand deposit location (denoted by the green circle).

Figure 3-2 Satellite map image of silica sand deposit location [82]

3.4 Sample preparation

Natural silica sand taken from the deposit site contains a lot of impurities and contaminants. In order to reduce the undesired minerals and obtaining higher purity silica sand, several pre-milling processes are done. The processes involve are washing, drying and sieving.

3.4.1 Washing

The objective of washing process is to remove unwanted particles and materials such as impurities, clay and foreign objects. Any minerals or particles other than silica sand will be removed in this process. The silica sand is washed in water and filtered to remove large and unwanted objects.

3.4.2 Drying

The washed silica sand is then sun dried to eliminate moisture content. This process can also be done by putting the silica sand in oven at a temperature of 120°C for one hour. However, drying using oven is more expensive compared to sun-dried especially if it is done in a large scale.

3.4.3 Sieving

After the drying step, the silica sand is taken for sieving process. The purpose of sieving is to ensure that the silica sand used for all experiments have the same size. Sieving process also helps to eliminate large particles and impurities that are not detected in previous washing process. The silica sand is sieved to the size of between 425μm t0 600μm.

3.5 Equipments used

There are several equipments used that are essential in the research. The equipments are components of a ball milling mechanism. They are the ball mill machine, grinding balls and milling jars.

3.5.1 Ball mill

The ball mill used in this research is US Stoneware planetary ball mill. It is a low speed ball mill with maximum speed of 100 rpm. The ball mill operates by sun wheel rotation on which the milling jar is placed. The totally enclosed DC drive motors permit solid-state control of roll speed. This ball mill also has a capacity of two milling jars. Figure 3-3 shows the ball milling machine used in the research.

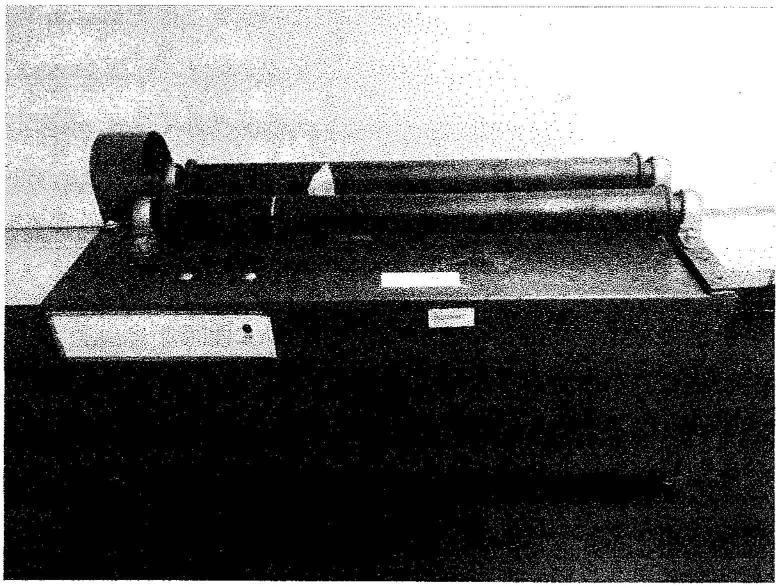


Figure 3-3 US Stoneware ball mill

3.5.2 Grinding balls

The grinding balls used in the research are made of zirconia. With a specific gravity of 5.5, equivalently sized zirconia grinding media generally will mill twice as fast as alumina. Zirconia grinding media is 1.6 times denser than alumina, has a hard nonporous surface that is chip resistance and easy to clean. It is unaffected by most chemicals, is nonconductive and nonmagnetic, and has outstanding resistance to mechanical and thermal shock. The zirconia grinding balls used have a diameter of 10 mm, each one weighs 3.14 g. Figure 3-4 shows zirconia grinding balls used in the experimental works.

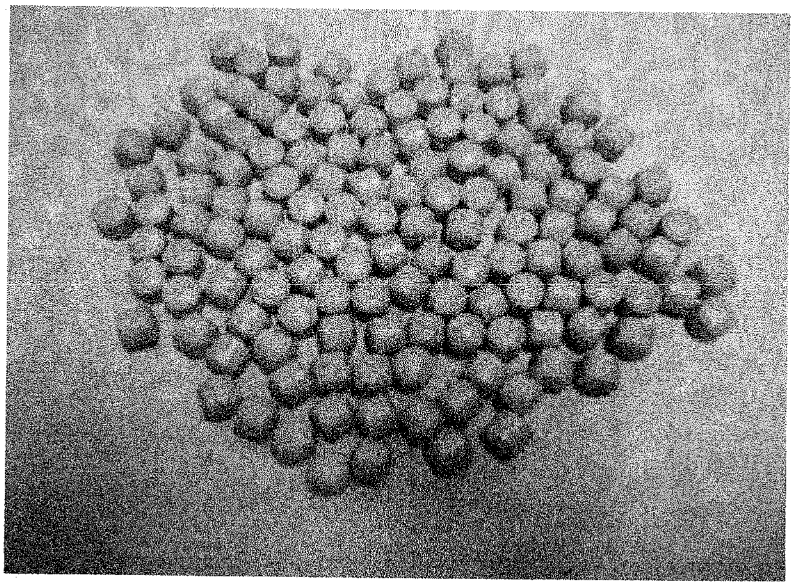


Figure 3-4 Zirconia grinding balls

3.5.3 Milling jars

The milling jars used are Roalox Alumina-fortified grinding jars. The ceramic jar bodies have been formulated to provide four times the wear rate of porcelain jars. Lower silica content cuts silica contamination by more than half. High-strength, impact resistant composition minimizes chipping and breakage. As shown in Figure 3-5, there are three sizes of milling jars available and used in this research.

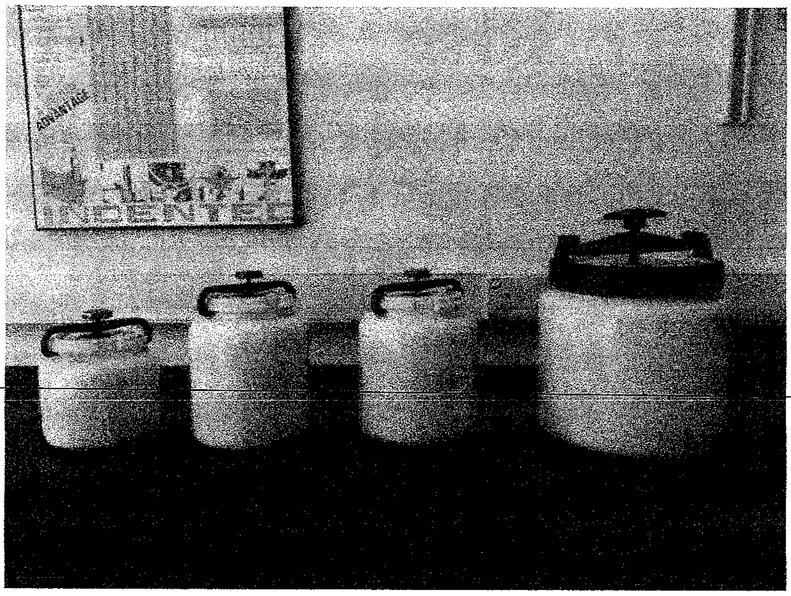


Figure 3-5 Milling jars

Table 3-1 shows the details of milling jars used such as volume, diameter, jar height and the weight of each jar.

Table 3-1 Milling jars specifications

Quantity	Jar size	Volume (ℓ)	Diameter (cm)	Jar height (cm)	Overall height (cm)	Weight (kg)
1	00	1.0	13.97	13.97	17.15	2.27
2	0	1.8	14.92	18.415	22.23	3.18
1	1	5.6	22.54	21.59	29.21	9.53

3.6 Research activities

As stated before, during sample preparation, the silica sand has been sieved to a size of between 425μm to 600 μm. The silica sand is then milled for 10 hours. For every two hours of milling, the silica sand will be sieved and dried in oven at a temperature of 120°C for 1 hour. Sieve sizes used are 425 μm, 212 μm, 150 μm and 63 μm. Sieving is not only important to control the size distribution of samples, it also can helps to filter out impurities and hard agglomerates which are not broken during milling process. Flow chart of research activities is shown in Figure 3-6.

3.7 Analysis

Grain sizes, median particle size (D50) and specific surface area (SSA) are usually used to assess the ball milling results [48]. D50 and SSA were measured by using particle size analyzer [48][51][72]. Scanning Mobility Particle Sizer (SMPS) was used to measure particle size and size distribution in the range of 3-1000 nm [49]. Acoustic particle sizer can also perform particle size measurement using 1-100 MHz frequency range. Particle in the size range of 10 nm to 100 μm can be measured using this equipment [49]. Particle size in nanoscale can be measured using transmission electron microscope (TEM) as well [49]. Other than the methods mentioned, Avettand-Fenoel used laser diffractometry to measure the particle size [75].

Scanning electron microscopy (SEM) [48][51][59] and transmission electron microscopy (TEM) were used to observe the microstructure and morphology of the milled WC-Co particle [51][58][69]. X-ray diffraction (XRD) analysis indicates the phase of milled products [13][15][20][35] Chemical analysis of the samples can be done using energy dispersive X-ray spectrometer (EDX) [53].

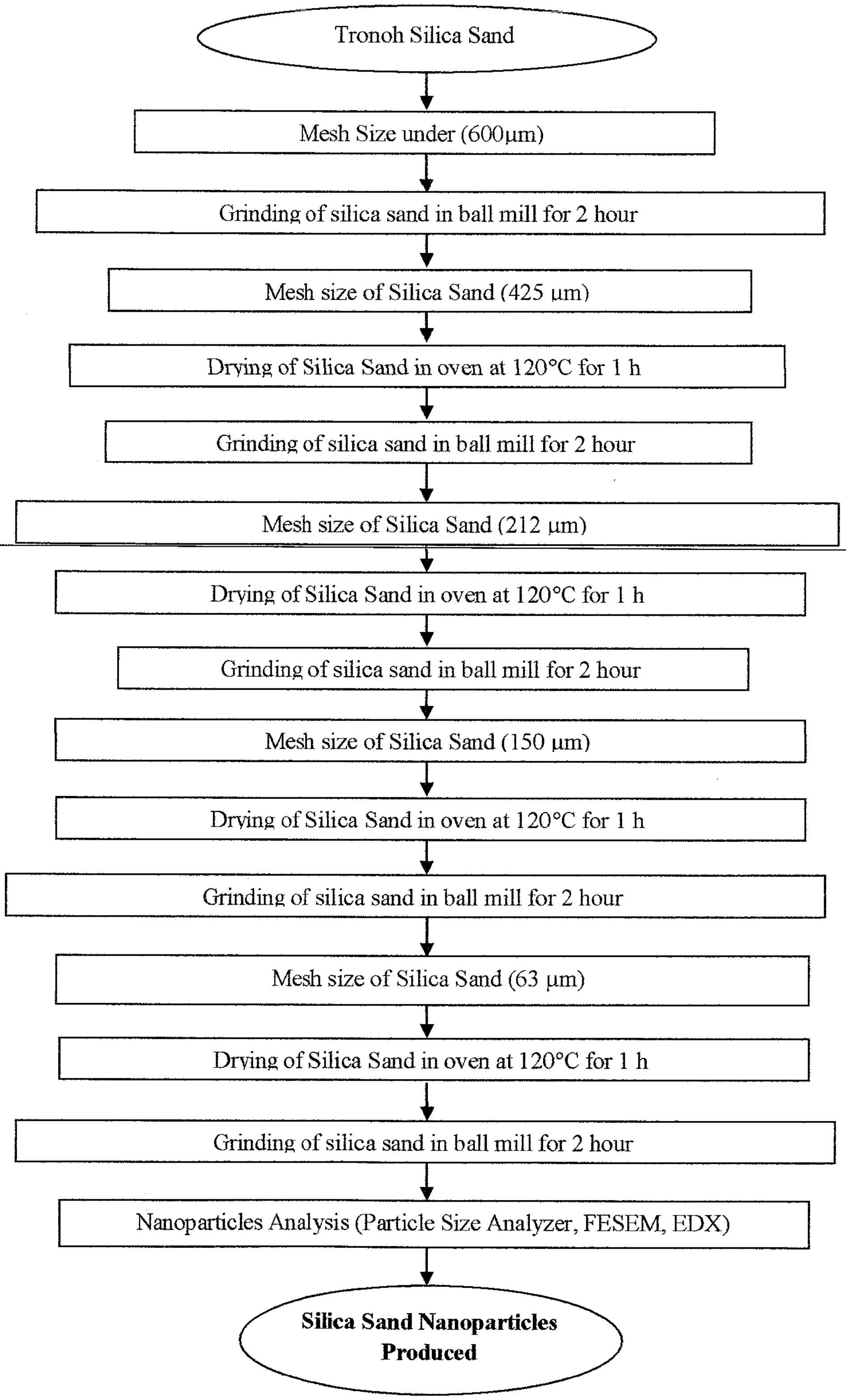


Figure 3-6 Flow charts of research activities

3.7.1 Particle Size Analyzer

The particle size analyzer used in this research is Malvern Instruments Mastersizer 2000. The Mastersizer 2000 uses laser diffraction technique to measure the size of particles. This is done by measuring the intensity of light scattered as a laser beam passes through a dispersed particulate sample. This data is then analyzed to calculate the size of the particles that created the scattering pattern. The results shown by particle size analyzer are for example the d(0.1), d(0.5), D[3,2], D[4,3], specific surface are, span and uniformity. D(0.1) is the size of particle below which 10% of sample lies. D(0.5) represents the size in microns at which 50% of the sample is smaller and 50% is larger. It is known as Mass Median Diameter (MMD). Surface area mean diameter, D[3,2] is also known as Sauter mean diameter. The Sauter mean diameter is important in calculations where the active surface area is important such as in fuel combustion and catalysis. The volume mean diameter, D[4,3] is known as De Broncker mean diameter. Monitoring the D[4,3] value will emphasize on detection of large particles. The specific surface area (SSA) is the total area of particles divided by total weight. The specific surface area increases as particles size decreases. Span is the measurement of the distribution width. The narrower the distribution, the smaller the span becomes. Uniformity measures the absolute derivation from the median. Figure 3-7 shows the particle size analyzer used in this research.

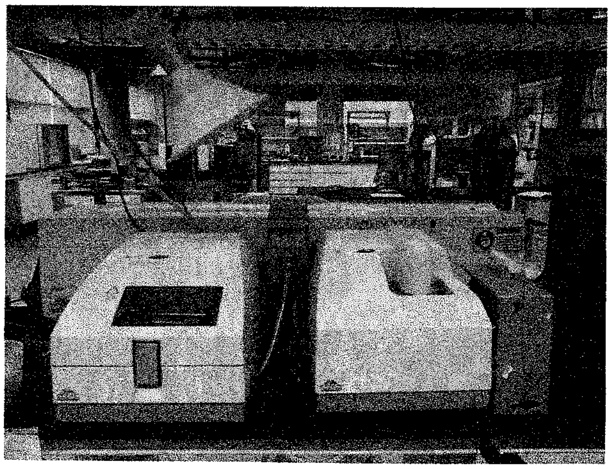


Figure 3-7 Malvern Instruments Masterizer 2000

3.7.2 Field Emission Scanning Electron Microscopy (FESEM)

The Field Emission Scanning Electron Microscopy (FESEM) used is the model of SUPRA 55VP and manufactured by Carl Zeiss AG Company. FESEM with ultra-high resolution imaging is designed to fulfill the requirements of analyzing up to nano-scale surface structure and morphology of solids. A well-defined electron beam impinges on the specimen and leads to generation of secondary electrons and characteristic X-rays. These electrons can be detected by suitable detectors and give information about the surface structure and morphology of the specimens. The characteristics X-rays generated are used for identification of different elements present in the specimen by energy dispersive spectrometer (EDS). Figure 3-8 shows the FESEM used in this research. Figure 3-8 shows the FESEM machine used.

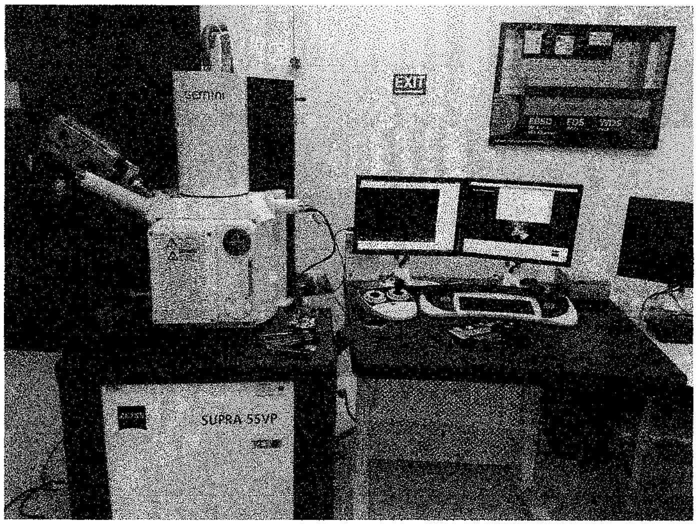


Figure 3-8 Carl Zeiss 55VP FESEM

3.7.3 Energy Dispersive X-ray analysis (EDX)

Energy Dispersive X-ray analysis (EDX), also referred to as EDS or EDAX, is an x-ray technique to identify the elemental composition of materials. EDX systems are attached to SEM, FESEM or TEM instruments where the imaging capability of the microscope identifies the specimen of interest. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed.

3.8 Parameters identification

There are a number of parameters associated with the ball milling process. Identification of these parameters is crucial to obtain the best milling setup. Setting the optimum parameters for milling process will ensure a higher quality output. Table 3-2 lists the parameters that were tested in previous works.

It can be observed from Table 3-2 that the parameters that have been tested most for optimization are the rotation speed and milling time. This indicates that these two parameters play an important role in determining the effectiveness of the milling. As supported by Simoes [83], ball to powder weight ratio is recognized as one of the most influential parameters, alongside milling time and rotation speed [83]. Zhang [48] believed that the volume of milling medium is the most influential parameter, followed by the rotation speed [48].

Table 3-2 Parameters tested in nanoparticles production by ball milling from previous works

Ref.	Parameter					
	BPR	Balls size	Type of milling medium	Rotation speed	Milling time	Grinding balls material
[48]	✓	✓	✓	✓		
[50]	✓			✓	✓	
[51]	✓				✓	✓
[52]				✓		
[55]				✓	✓	
[62]					✓	✓
[66]				✓		
[69]					✓	

[70]			✓		✓	
[71]		✓		✓	✓	
[74]					✓	
[76]				✓	✓	
[77]		✓		✓		
[78]	✓			✓	✓	
[79]					✓	

3.8.1 Rotation speed

According to Zhang [48], increasing rotation speed accelerates milling efficiency. Higher rotation speed can improve grain size and particle size reduction. Increasing rotation speed will increase the speed with which the balls move. Above critical speed, the balls will be pinned to the jar inner walls and will not fall down to exert impact force. Therefore, maximum speed should be just below the critical value so that the balls will fall down from maximum height to produce maximum collision energy [84].

3.8.2 Milling time

Suryanarayana [85] stated that the time required varies depending on the ball to powder ratio, intensity of milling, type of mill and milling temperature. For each parameters combination and particular powder system, the milling time has to be decided. However, it should be realized that contamination level increases and some undesirable phases will form if powder is milled for times longer than required. The powder should be milled just for the required duration and not any longer.

3.8.3 Ball to powder weight ratio

Zhang [48] proposed that the best ball to powder weight ratio is 15:1 for grain size reduction and 20:1 for particle size reduction. Othman [51] however believed that for stainless steel grinding balls, BPR of 10:1 produces finer powders compared to 20:1 due to optimum for collision, resulting in higher impact energy

3.9 Parameters optimization

Optimization of ball milling parameters is crucial for the efficiency of grain size and particle size reduction in the fabrication of nanostructured powder [48]. Taguchi technique provides a simple, efficient and systematic approach to determine optimal parameters in manufacturing process. It is being used to study the entire parameters space with small number of experiments rather than testing all possible combinations. Statistical analysis of variance (ANOVA) can then be performed to identify statistically significant parameters [48].

From previous works, the BPR that is commonly used is in the range of 10:1 to 20:1 [69]. However, there is no conclusive decision on the best BPR since some works got the best result when using BPR of 20:1 while some got the best result when using BPR 10:1. Other works stated that the BPR should be at least 15:1 to yield the best result [62]. Therefore, the BPR used in this research are 10:1, 15:1 and 20:1. For volume of milling jar, there are three sizes available in the lab which is 5.6 ℓ, 1.8 ℓ and 1.0 ℓ. All of the milling jar sizes will be used in this research. For the milling speed, since previous works usually used high speed ball milling which is more than 100 rpm, it is difficult to know the best speed for low speed ball mill. Since higher speed results in higher collision between grinding balls and powder, therefore three highest speeds will be used which are 100 rpm, 95 rpm and 90 rpm [70]. Table 3-3 lists the parameters and levels for each parameter that will be tested.

Table 3-3 Parameters selected and levels for each parameter

Parameter	Level 1	Level 2	Level 3
Ball to powder weight ratio (BPR)	20:1	15:1	10:1
Volume of milling jar	5.6 ℓ	1.8 ℓ	1.0 ℓ
Milling speed	100 rpm	95 rpm	90 rpm

Both the number of parameters and levels are three. Referring to the parameter design orthogonal array selector shown in Table 3-4, the selected array is Level 9 (L9) Array.

Table 3-4 Parameter design orthogonal array selector [73]

		Number of parameters (P)							
		2	3	4	5	6	7	8	9
Number of Levels	2	L4	L4	L8	L8	L8	L8	L12	L12
	3	L9	L9	L9	L18	L18	L18	L18	L27
	4	L’16	L’16	L’16	L’16	L’32	L’32	L’32	L’32
	5	L25	L25	L25	L25	L25	L50	L50	L50

Table 3-5 shows the L9 Array selected. Note that L9 Array has 4 parameters considered. Since the research only considers 3 parameters to be used for Taguchi method experimental design, the column representing Parameter 4 (P4) can be deleted [73]. Table 3-6 shows the experiment numbers and actual parameters levels inserted into L9 Array.

Table 3-5 Level 9 Array

Experiment	Parameter 1	Parameter 2	Parameter 3
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

Table 3-6 Actual parameters and levels in L9 Array

Experiment	BPR	Volume of Milling Jar	Rotation Speed
1	20:1	5.6 ℓ	100 rpm
2	20:1	1.8 ℓ	95 rpm
3	20:1	1.0 ℓ	90 rpm
4	15:1	5.6 ℓ	95 rpm
5	15:1	1.8 ℓ	90 rpm
6	15:1	1.0 ℓ	100 rpm
7	10:1	5.6 ℓ	90 rpm
8	10:1	1.8 ℓ	100 rpm
9	10:1	1.0 ℓ	95 rpm

3.9.1 Preliminary Results

Results from the sets of experiments obtained by using Taguchi method of orthogonal array will be further analyzed using SN ratio and ANOVA technique. Analysis using SN ratio and ANOVA will determine which parameter is the most significant parameter compared to the others. Analysis on the samples from 9 experiments constructed using the Taguchi method of orthogonal array have been done using Particle Size Analyzer machine (Malvern Instruments Mastersizer 2000). The results from particle size analyzer indicate the size distribution for each sample. Particle size for each sample is selected for comparison and analysis. Table 3-7 shows experiments numbers and the particle size for each experiments obtained using the analysis from particle size analyzer.

Table 3-7 Preliminary experiments and results

Experiment	BPR	Jar Volume	Rotation Speed	Mean Particle Size (µm)
1	20:1	5.6 ℓ	100 rpm	2.999
2	20:1	1.8 ℓ	95 rpm	2.880
3	20:1	1.0 ℓ	90 rpm	2.893
4	15:1	5.6 ℓ	95 rpm	5.244
5	15:1	1.8 ℓ	90 rpm	4.630
6	15:1	1.0 ℓ	100 rpm	4.951
7	10:1	5.6 ℓ	90 rpm	10.040
8	10:1	1.8 ℓ	100 rpm	7.969
9	10:1	1.0 ℓ	95 rpm	6.343

3.9.2 Signal-to-noise ratio analysis

To determine the effect of each parameter on the output, the signal-to-noise ratio, or the SN number, needs to be calculated for each of the experiment conducted. In the following equation, y_i is the mean value and s_i is the variance. y_i is the value or the result for each experiment [36].

$$SN_i = 10\log\ (\bar{y}_i^2 / s_i^2)$$

Where,
$$\bar{y}_i = 1/N_i \sum_{u=1}^{N_i} y_{i,u}$$

$$s_i^2 = (1/N_i - 1)\sum_{u=1}^{N_i}(y_{i,u} - \bar{y}_i)$$

Where, *i* is the experiment number, *u* is the trial number and N_i is the number of trials for experiment *i*. For minimizing the performance characteristics, the following Eq. (1) of SN ratio should be used. SN ratio value calculated for each experiment is shown in Table 4.

$$SN_i = -10\log \sum_{u=1}^{N_i} y_u^2 / N_i \qquad (1)$$

Using the SN ratio equation as shown in Eq. (1), SN ratio is calculated for each experiment. The values are shown in Table 3-8.

Table 3-8 SN ratios for each experiment

Experiment	BPR	Volume of milling jar	Milling Speed	SN ratio
1	1	1	1	-9.5406
2	1	2	2	-9.1881
3	1	3	3	-9.2160
4	2	1	2	-14.3935
5	2	2	3	-13.3123
6	2	3	1	-13.8945
7	3	1	3	-20.0350
8	3	2	1	-18.0288
9	3	3	2	-16.0463

After SN ratio for each experiment has been calculated, the average SN value is calculated for each parameter and level. After the SN ratio values are calculated for each parameter and level, the values are tabulated into SN Response Table as shown in Table 3-9 and the range R (R = highest SN – lowest SN) of SN for each parameter is calculated. The larger the R values for a parameter, the larger the effect of the parameter on the process. Same change in signal causes larger effect on the output variable [73].

Table 3-9 SN Response Table

Level	Ball to powder weight ratio	Volume of milling jar	Rotation speed
1	-9.3149*	-14.6563	-13.8213
2	-13.8667	-13.5097	-13.2093*
3	-18.0367	-13.0222*	-14.1877
Δ	8.7218	1.6341	0.9784
Rank	1	2	3

* Optimum parameter level

From the SN Response Table above, the ball to powder weight ratio is the most influential parameter followed by volume of milling jar and rotation speed.

It is known from Table 3-10 that for ball to powder weight ratio parameter, level 1 (BPR 20:1) is the optimum level, for volume of milling jar, the optimum level is level 3 (Volume 1.0 ℓ) while for milling speed, level 2 (95 rpm) is the optimum level.

Table 3-11 lists the summary of optimum parameter levels calculated using SN ratio and ANOVA. From the analysis of the results, the optimum parameters for producing silica nanoparticles using low speed ball mill have been identified. The next step in this research is lab scale production of silica sand nanoparticles by using the optimum parameters.

Table 3-11 Optimum Parameters

Parameter	Level	Description
Ball to powder weight ratio	1	20:1
Volume of milling jar	3	1.0 ℓ
Rotation speed	2	95 rpm

3.10 Chapter Summary

This chapter discussed on the methodology used in the research. This includes sample preparations, equipments used and research activities. The analysis done to the silica sand nanoparticles produced is also thoroughly explained. This chapter also showed preliminary results and analysis of the experiments to determine optimum parameters.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Chapter Overview

In this chapter, the results from research works are presented and discussed. These results include the particle size and size distribution analysis, microstructure analysis from FESEM and chemical composition using EDX. Problems occurred during experiments are also ~~presented together with the preventive measures taken.~~

4.2 Lab-scale production

After the optimum parameters have been identified from previous analysis, silica sand nanoparticles can be produced in lab-scale production. The most important aspect to be observed in this lab-scale production is the ability to produce silica sand nanoparticles consistently. Only when the lab-scale production proved to be able to produce silica sand nanoparticles consistently that the research can be scale-up to mass production and commercialization stage.

A total of 20 experiments have been done to evaluate the ability to produce silica sand nanoparticles repeatedly. Samples from all 20 experiments have been analyzed using Malvern Instruments Particle Size Analyzer for its size distribution analysis. Table 4-1 below shows the results for lab-scale production of silica sand nanoparticles.

Table 4-1 Lab-scale production results

No.	Particle Size Analysis						
	d (0.1)	d (0.5)	SSA (m^2/g)	SWM D[3,2]	VWM D[4,3]	Span	Uniformity
1	45 nm	249 nm	50.90	117 nm	366 nm	3.376	1.05
2	44 nm	238 nm	52.85	113 nm	358 nm	3.504	1.09
3	43 nm	238 nm	54.03	111 nm	353 nm	3.448	1.08
4	43 nm	223 nm	54.83	109 nm	342 nm	3.590	1.12
5	42 nm	209 nm	57.46	104 nm	322 nm	3.598	1.13
6	42 nm	195 nm	58.27	103 nm	310 nm	3.731	1.16
7	41 nm	198 nm	59.14	101 nm	303 nm	3.538	1.11
8	41 nm	196 nm	59.25	101 nm	301 nm	3.536	1.11
9	45 nm	269 nm	50.00	119 nm	393 nm	3.364	1.06
10	45 nm	261 nm	50.23	119 nm	388 nm	3.443	1.08
11	41 nm	187 nm	60.00	101 nm	294 nm	3.650	1.14
12	41 nm	189 nm	59.73	105 nm	293 nm	3.607	1.13
13	42 nm	201 nm	57.91	103 nm	312 nm	3.632	1.13
14	42 nm	202 nm	57.88	202 nm	314 nm	3.621	1.13
15	41 nm	183 nm	60.6	99 nm	288 nm	3.649	1.14
16	41 nm	172 nm	61.67	97 nm	279 nm	3.809	1.18
17	41 nm	181 nm	60.89	98 nm	287 nm	3.680	1.15
18	41 nm	166 nm	62.48	96 nm	274 nm	3.923	1.21
19	42 nm	191 nm	59.11	101 nm	299 nm	3.634	1.13
20	42 nm	204 nm	58.11	103 nm	204 nm	3.496	1.10

The d (0.1) for all production batches clearly shows that nanoparticles of less than 50nm have been consistently produced, with the size ranges between 41-45 nm. From Table 4-1, the median size of particles produced is around 200 nm, with the size ranges between 166 to

249 nm. As can be observed in Table 4-1, large particles with size up to 393 nm have been detected which confirms the inconsistent size distribution of the sample. SSA of all batches ranges around 50-60 m^2/g, indicating large specific surface area particles have been produced. However, the SSA values will be significantly higher if large size particles can be prevented. Table 4-1 shows high values of span resulted from big and inconsistent particles size. Since the median values are high which is around 200nm, the particles have a high uniformity as the sizes did not differ by much compared to the median value. Figure 4-1 shows the d(0.1) and d(0.5) results for lab-scale production.

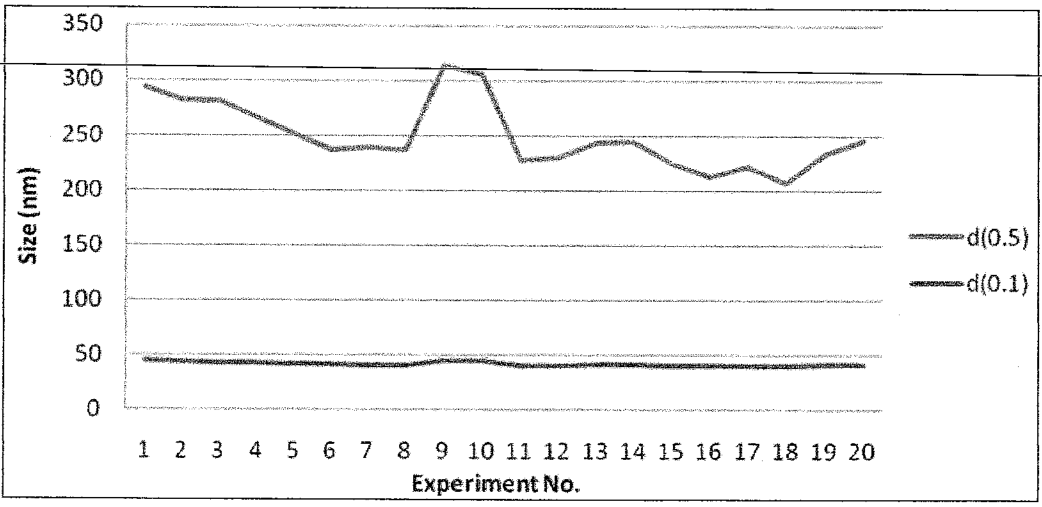


Figure 4-1 Lab-scale production d (0.1) and d (0.5) results

From Figure 4-1, the graph shows that there are two main sizes in all the samples analyzed. Larger size group is in the range of between 200 nm and 325 nm. The smaller size group is slightly below the 50 nm mark. Unlike the smaller size group where the readings are almost the same, larger size group indicates a significantly different readings. Ranging from 166 nm until 269 nm, the larger size group is the result of agglomerated silica sand powders that were sticked to the inner wall of milling jar. The agglomerated powders did not receive further size reduction during milling process. The following Figure 4-2 shows the particle size distribution for lab-scale production of batch 18. The graph shows volume percentage versus the particle size.

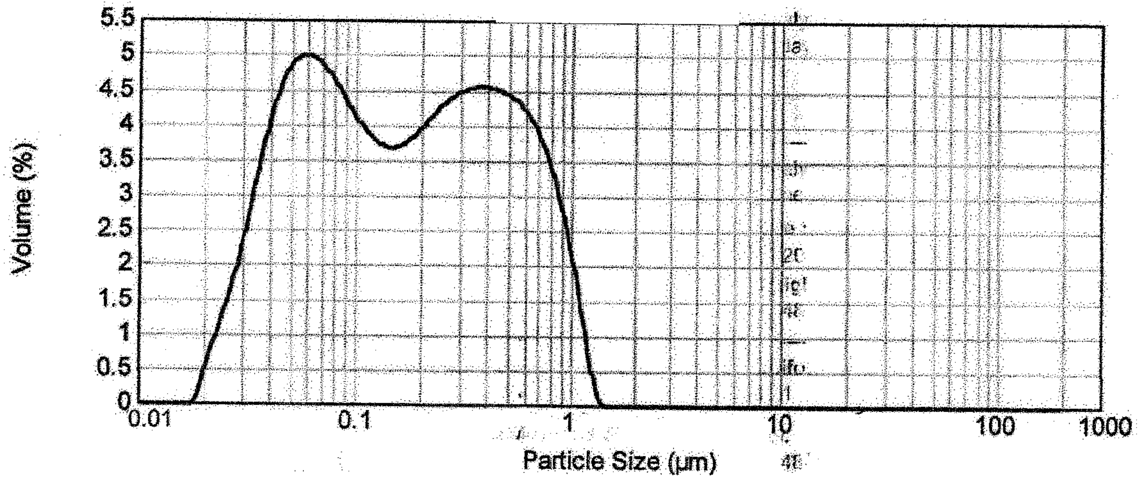


Figure 4-2 Lab scale production batch 18

The particle size distributions for all 20 experiments are then compared in Figure 4-3. From this comparison, the overall particle size distribution from lab-scale production is observed and evaluated. Figure 4-3 shows the comparison of all 20 experiments size distribution graph. It can be seen that there are two dominant sizes for all 20 experiments with Experiments 1, 2, 3, 4, 9 and 10 indicate that the larger size group is more dominant than the smaller size group. Experiments 16 and 18 indicate that the smaller size group is slightly more dominant than the larger one. The rest 12 experiments although the larger size group is slightly higher than the smaller group, the percentage difference between the two groups is no higher than 0.5 %.

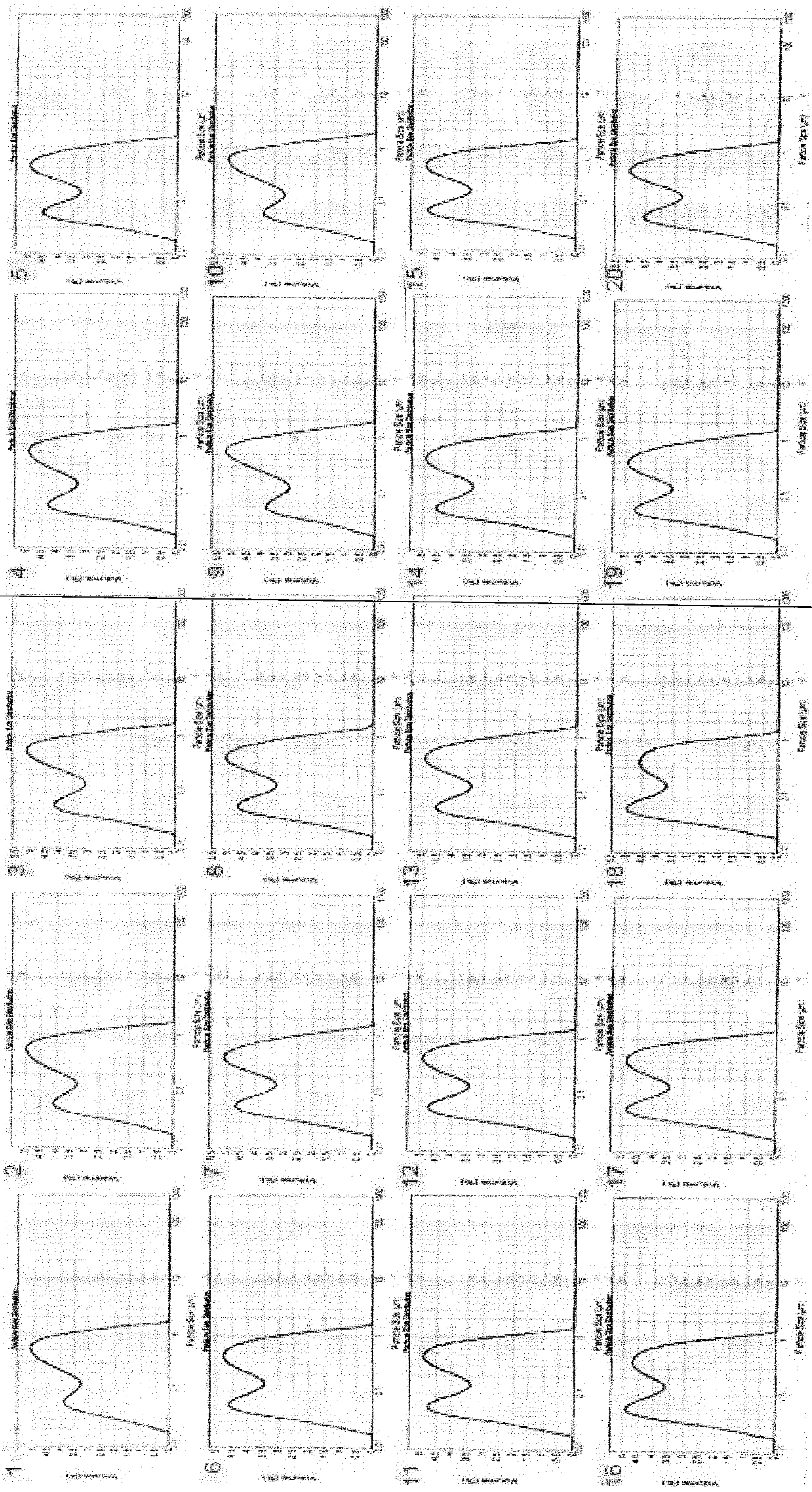


Figure 4-3 Comparison of all 20 experiments on particle size distribution of silica sand

4.2.1 Lab-scale production problems identification

Although the lab-scale experiments have proved the ability to produce silica sand nanoparticles, there are some issues regarding the results obtained. Identifying the problems occurred is crucial so that appropriate measures can be taken to produce a better results.

(a) Bimodal graph distribution

The desired result is normal distribution graph which contains only one peak. However, results from lab-scale production showed that bimodal graph distribution of two peaks are formed for all 20 experiments done. To obtain a normal or skewed graph distribution, the peak that represents higher particles size need to be eliminated or reduced.

(b) High intensity of particles not in nanometer region

From the size distribution graph shown in Figure 4-1, there are two peaks formed in lab-scale production. One peak is in the nanometer region at around 60 nm while the other peak is around 400 nm. The large size particles are the effect of agglomerations during milling process. Reducing the agglomeration problem will reduce the intensity of large particles.

(c) High d (0.5) value

D (0.5) value represents the median size of a graph distribution. In this research, median size in nanometer region is desired. However, the lab-scale production results showed that the median sizes are around 200 nm, slightly higher than the preferred 100 nm mark. Median size is affected by the presence of large size particles. Reducing these particles will help to lower down the d (0.5) value.

4.2.2 Preventive measures

The problems identified from lab-scale production are all pointing to a root cause; the agglomeration of silica sand particles during milling process. Agglomeration is a common problem in milling process. The agglomeration usually happens when the silica sand particles are sticked onto the inner wall of the milling jar. Agglomerated particles will not undergo further size reduction and this is the reason for having a bimodal graph distribution as large size particles are present. The large size agglomerated particles also will affect the median size or d (0.5) values to be higher than expected. Therefore, to counter the problem, agglomeration during milling process needs to be overcome. This can be done by scrapping the sticked silica sand particles on the inner wall of milling jar from time to time. For improvement on the lab-scale production results, the scrapping process is done for every 30 minutes of milling.

4.3 Improvement to the lab-scale experiments

Since agglomeration is the main problem during lab-scale production, improvement experiments are done to obtain better results. 10 experiments have been done using the same methods as in the lab-scale production but with an addition of scrapping process for every 30 minutes of milling. The particle size analysis results of improvement experiments are shown in Table 4-2.

Table 4-2 Improvement on lab-scale production results

No.	Particle Size Analysis						
	d (0.1)	d (0.5)	SSA (m^2/g)	SWM D[3,2]	VWM D[4,3]	Span	Uniformity
1	42 nm	51 nm	158.27	89 nm	136 nm	3.183	1.05
2	42 nm	50 nm	152.85	87 nm	158 nm	3.430	1.09
3	41 nm	49 nm	159.25	81 nm	143 nm	3.355	1.08
4	41 nm	44 nm	159.14	71 nm	132 nm	3.420	1.12

5	42 nm	51 nm	154.03	89 nm	122 nm	3.217	1.13
6	42 nm	47 nm	150.23	73 nm	140 nm	3.215	1.16
7	41 nm	49 nm	154.83	79 nm	133 nm	3.122	1.11
8	42 nm	48 nm	150.64	74 nm	131 nm	3.127	1.11
9	41 nm	50 nm	150.90	83 nm	133 nm	3.269	1.06
10	43 nm	44 nm	157.46	71 nm	148 nm	3.277	1.08

As can be viewed in Table 4-2, the d (0.5) value which represents the median size has been significantly reduced from a few hundred nanometers to less than 100 nm. This indicates that the average particle size have been successfully reduced to nanosize region. The specific surface area of nanoparticles produced has been increased to higher than 150 m^2/g as a result of overall particle size reduction. The surface weighted mean. D[3,2] and volume weighted mean, D[4,3] both show a lower values due to the elimination of large particles in the sample. The improvement experiments results also show that a narrower span has been achieved, reflecting a more uniform particle size distribution.

Compared to previous lab-scale experiments results (Table 4-1), the improvement experiments produce a single peak (normal distribution) instead of two peaks (bi-modal distribution). The bi-modal distribution from lab-scale productions are caused by agglomeration which produce unbroken large particles. As the agglomeration problem has been solved in the improvement experiments, the particles size are more uniform resulting to a normal distribution graph. Although the graph appears to be a normal distribution, it is slightly skewed to the right. This indicates that although a median particle size in nanometer range has been achieved, there are still particles larger than 100 nm exist. However, the percentage volume of these particles is significantly lower than in lab-scale productions and is not alarming. Figure 4-4 shows an example of particle size distribution produced from Improvement Experiment 7 while Figure 4-5 shows the particle size distribution results for all 10 Improvement Experiments.

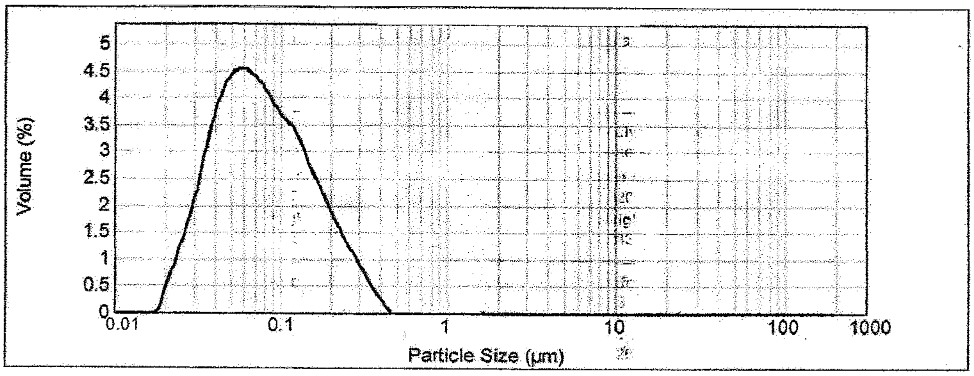


Figure 4-4 Particle size distribution graph for improvement on lab scale production Experiment 7

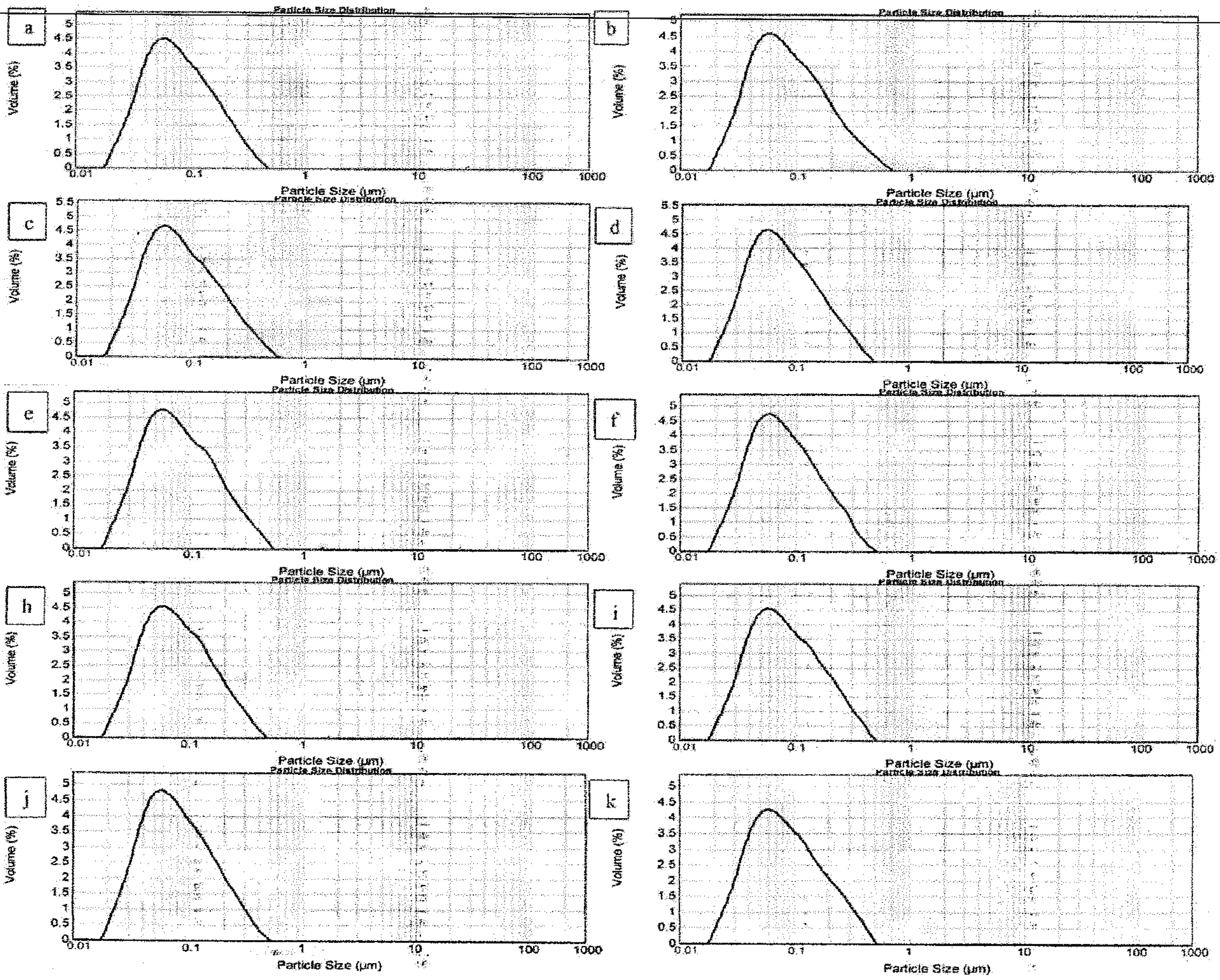


Figure 4-5 Particle size distribution for Improvement Experiments 1 to 10 ((a)-(j))

From the particle size distribution comparison showed by Figure 4-5, it can be seen that for all 10 Improvement Experiments done, a normal distribution graph are obtained with a slight skewed to the right. As the agglomeration problem has been overcome, the silica sand nanoparticles produced are more uniform in size and well below the 100 nm mark. Therefore, the Improvement Experiments have successfully produced better results and solved the problems encountered in lab-scale production.

4.4 Microstructural analysis

Figure 4-6 until Figure 4-8 represents FESEM results for Improvement Experiments 2, 5 and 8 at 200X and 100KX magnification. The FESEM analysis clearly confirmed the existence of silica sand nanoparticles of less than 100 nm. The nanoparticles formed have irregular shape with most of them are in the shape of cubic. Contrary to the chemical synthesis of nanoparticles, ball milling method hardly produces uniform and spherical shapes. The FESEM images also show that there is formation of agglomerates represented by large particles. However, these large particles are just slightly bigger than 100 nm and the occurrence is at a minimum level.

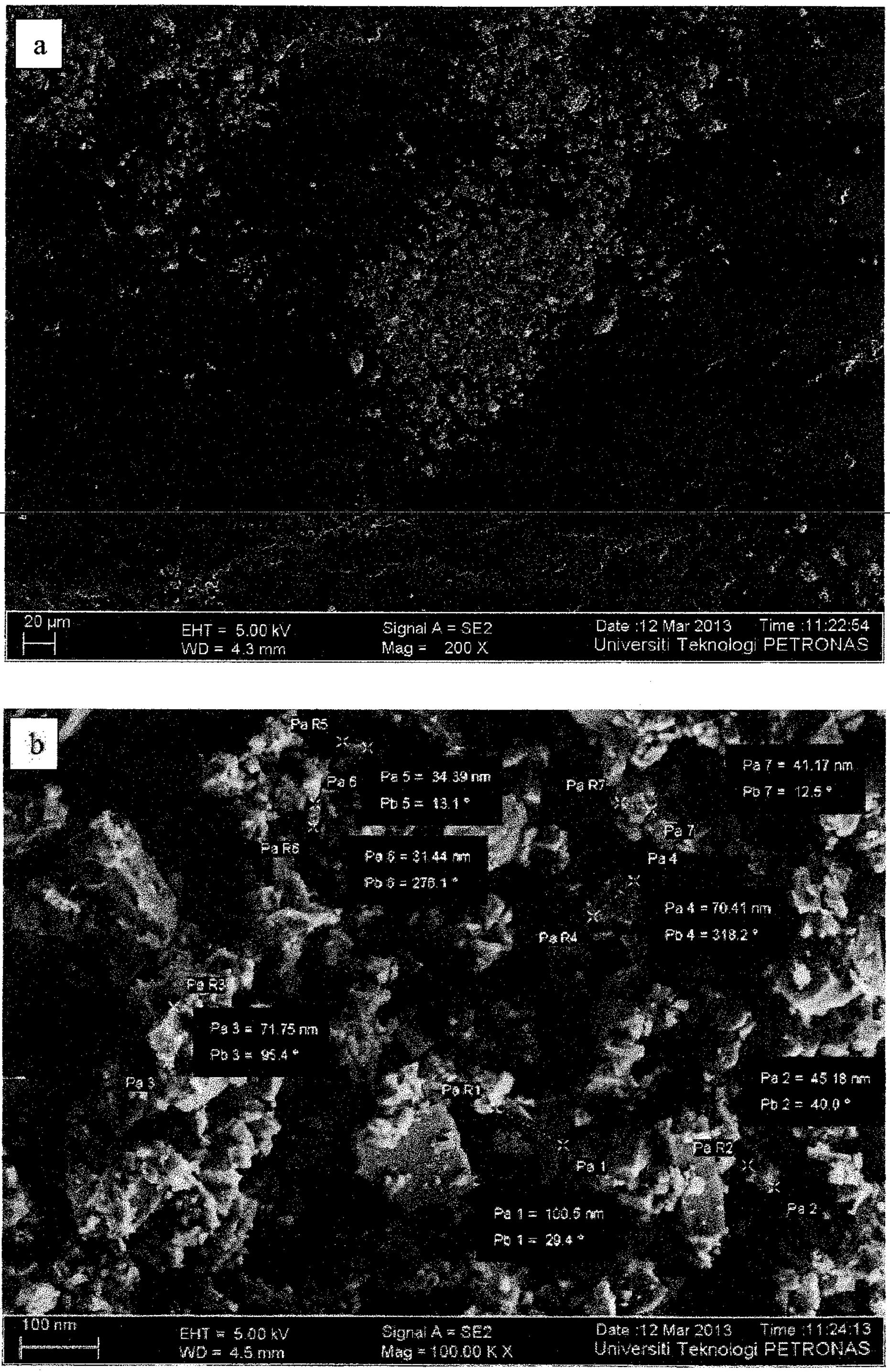


Figure 4-6 FESEM analysis of Improvement Experiment 2 (a) at 200X magnification, (b) at 100KX magnification

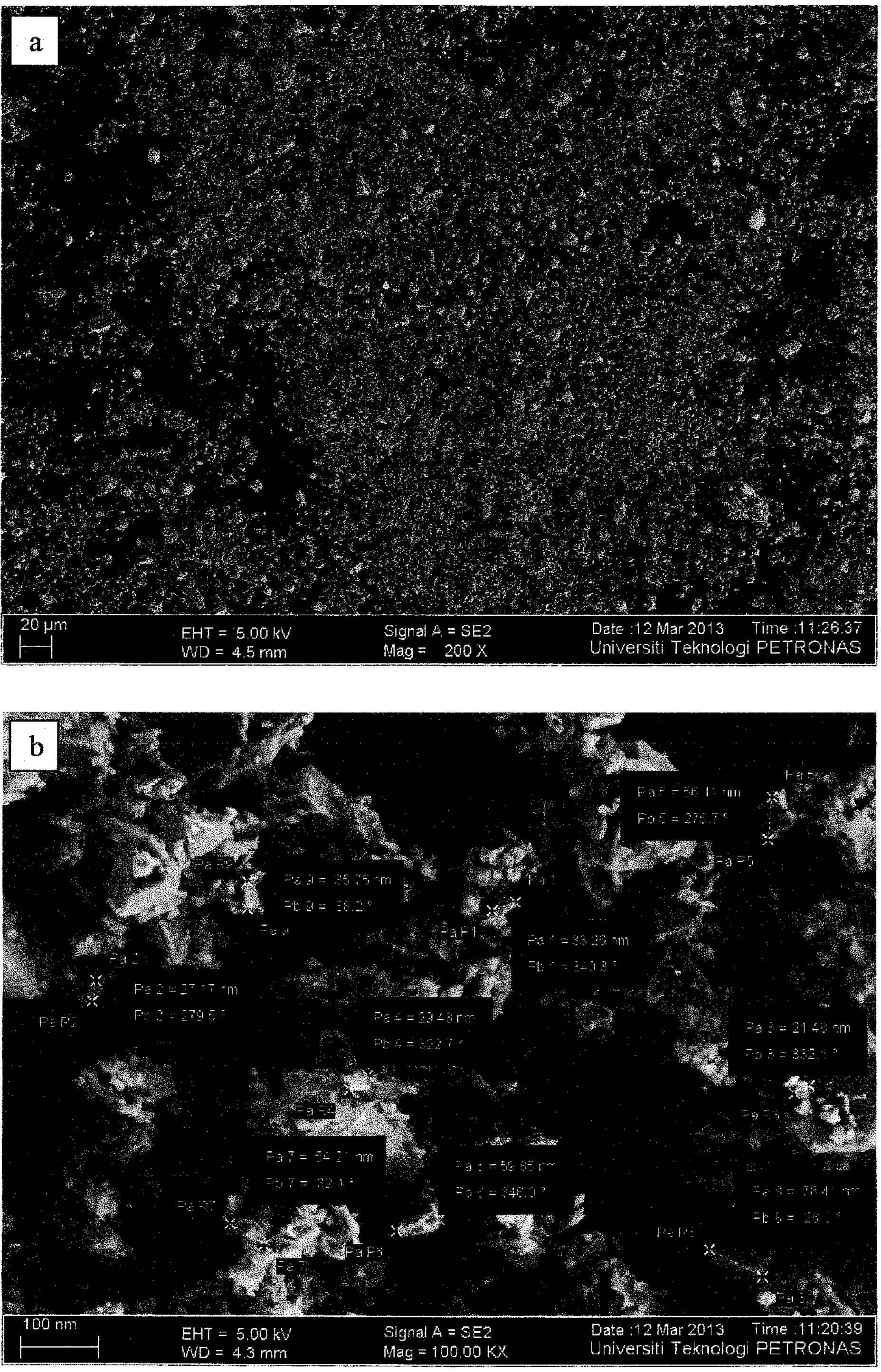


Figure 4-7 FESEM analysis of Improvement Experiment 5 (a) at 200X magnification, (b) at 100KX magnification

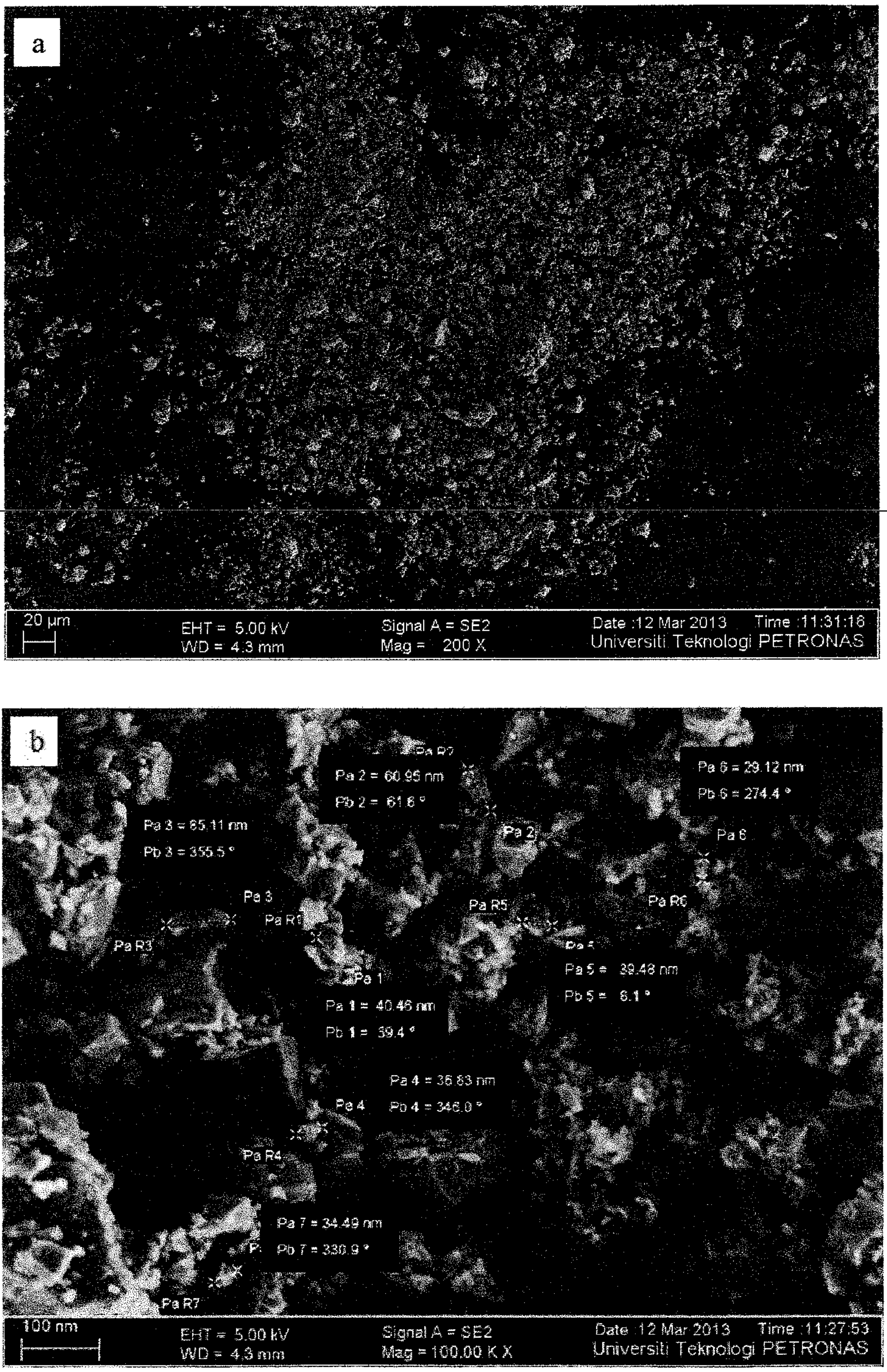
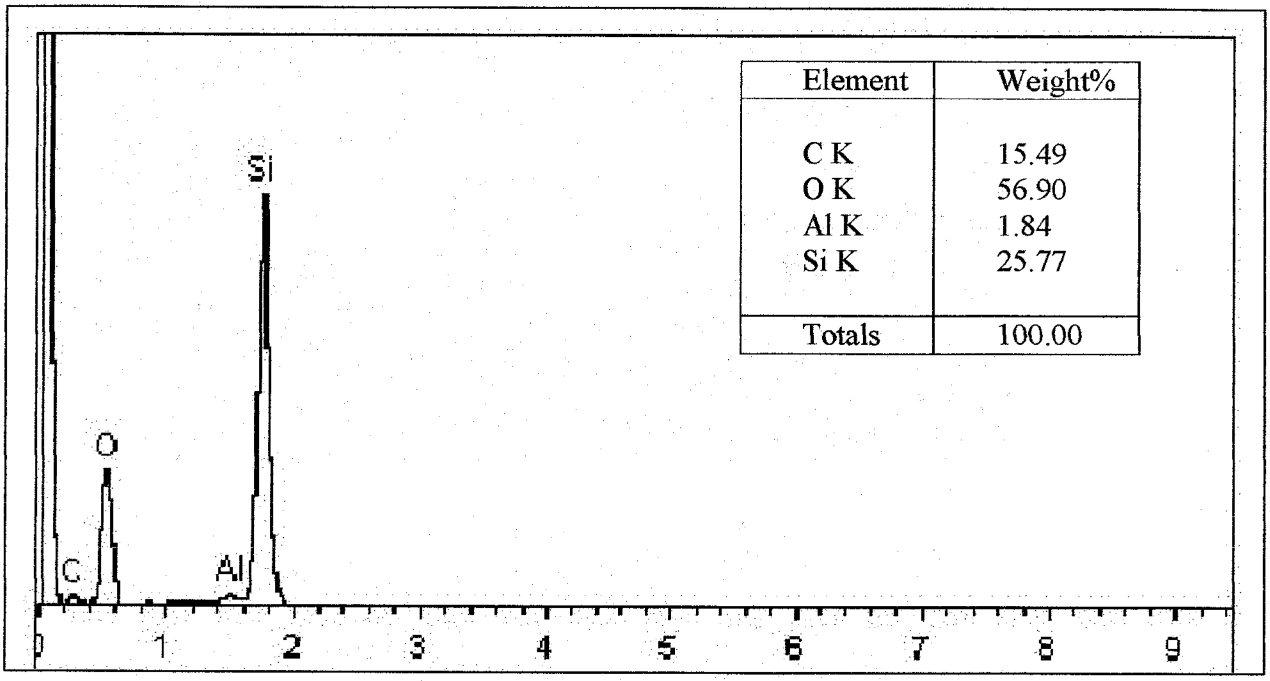


Figure 4-8 FESEM analysis of Improvement Experiment 8 (a) at 200X magnification, (b) at 100KX magnification

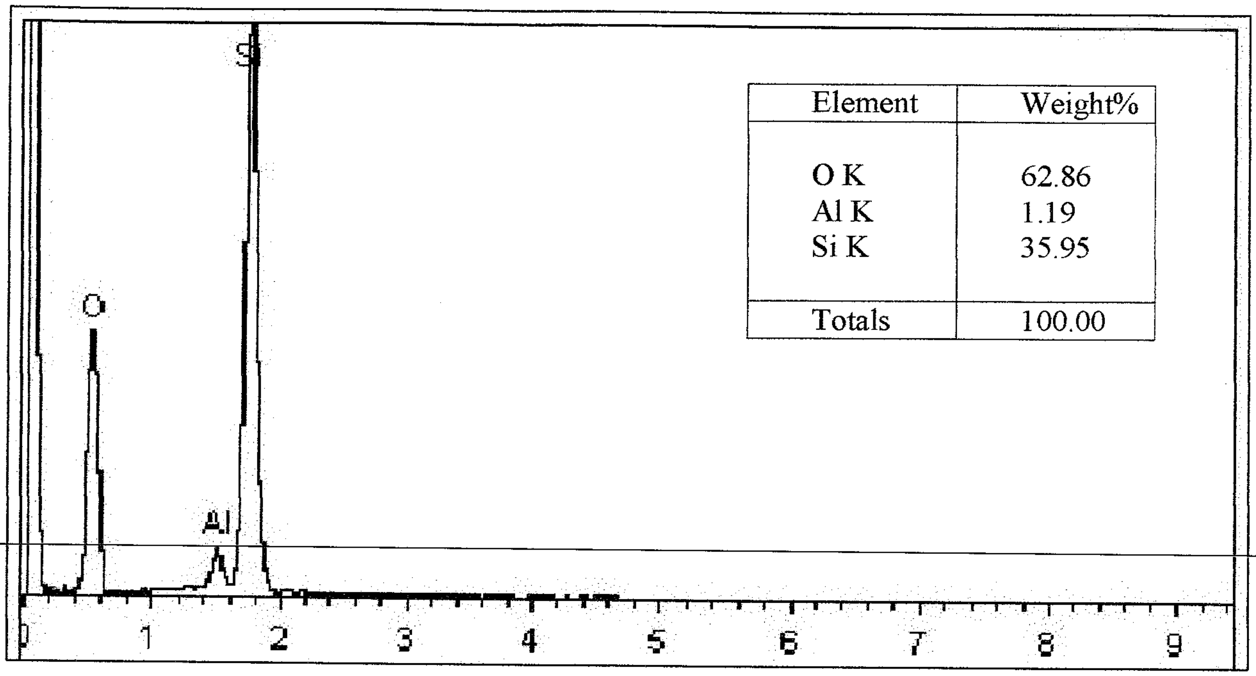
4.5 Chemical composition analysis

The chemical composition analysis using Energy Dispersive X-ray spectroscopy (EDX) results are shown in Figure 4-9 to Figure 4-12.



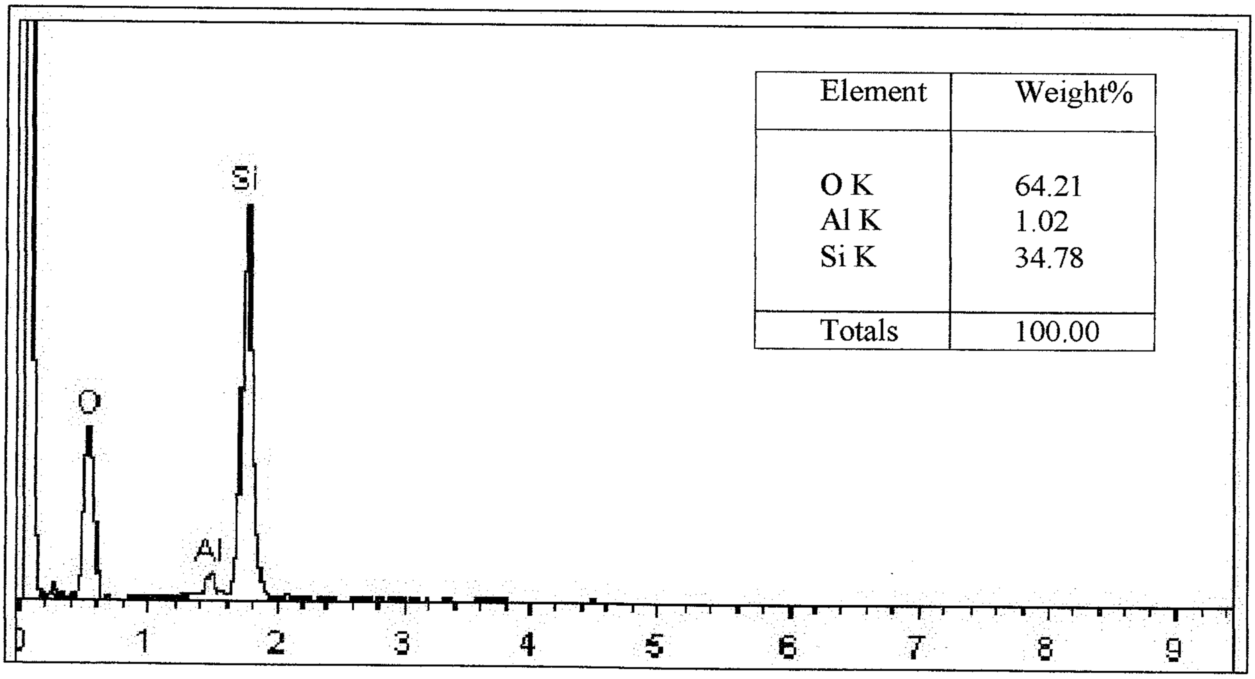
Element	Weight%
C K	15.49
O K	56.90
Al K	1.84
Si K	25.77
Totals	100.00

Figure 4-9 EDX analysis of raw unprocessed silica sand



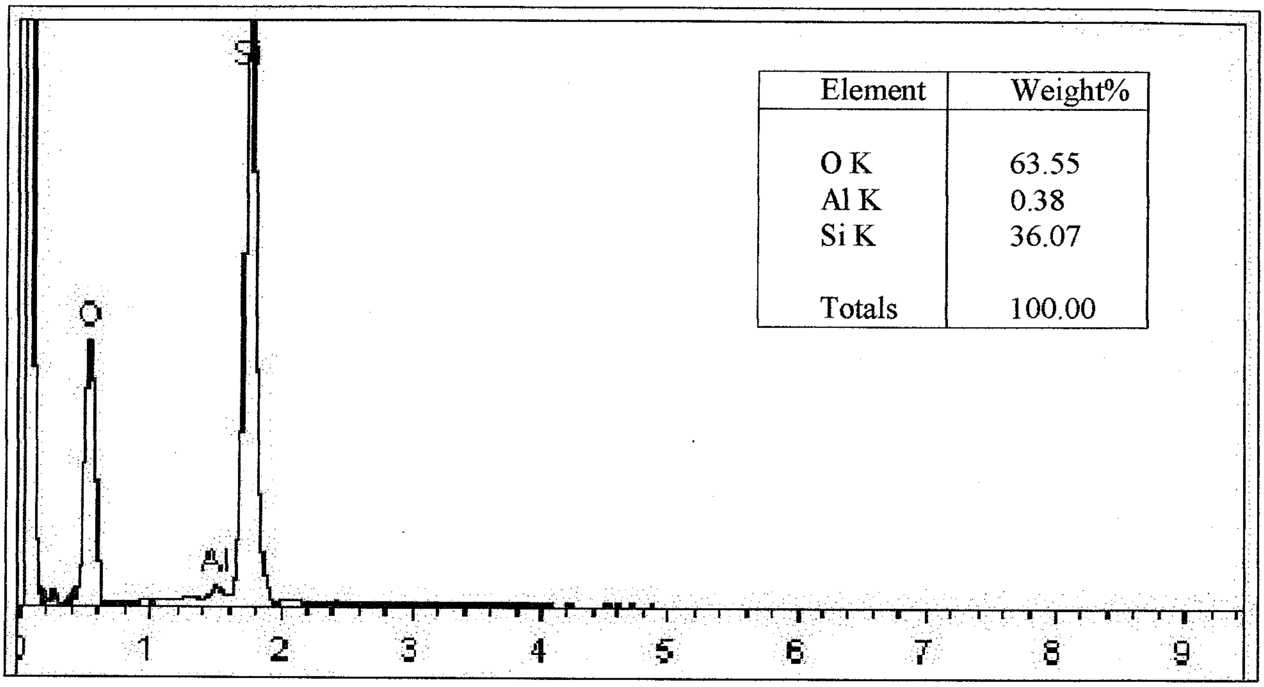
Element	Weight%
O K Al K Si K	62.86 1.19 35.95
Totals	100.00

Figure 4-10 EDX analysis of Improvement Experiment 2



Element	Weight%
O K Al K Si K	64.21 1.02 34.78
Totals	100.00

Figure 4-11 EDX analysis of Improvement Experiment 5



Element	Weight%
O K	63.55
Al K	0.38
Si K	36.07
Totals	100.00

Figure 4-12 EDX analysis of Improvement Experiment 6

To determine the purity of silica sand before and after the ball milling process, calculations to the element weight percentage are done.

Purity of raw silica sand = [25.77/ (25.77+1.84+15.49)] X 100%
= 59.79%

Purity of silica sand for Improvement Experiment 2 = [35.95/(35.95+1.19)] X 100%
= 96.80%

Purity of silica sand for Improvement Experiment 5 = [34.78/(34.78+1.02)] X 100%
= 97.15%

Purity of silica sand for Improvement Experiment 6 = [36.07/(36.07+0.38)] X 100%
= 98.96%

EDX analysis results obviously showed that the milling process helps to increase purity of silica content. The purity of raw silica sand is just 59.79%. However, after the silica sand has gone through the sieving and milling process, its purity significantly increases to more than 95% as shown in previous calculations. Other than that, raw silica sand contains carbon element. This carbon element has been successfully eliminated after 10 hours of milling. The elimination of impurities such as carbon is also the result of sieving process which was done gradually every 2 hours of milling. Sieving process eliminated impurities such as carbon as well as agglomerated silica sand. This has a significant contribution in producing more uniform silica sand nanoparticles with high silica purity.

4.6 Chapter Summary

This chapter has presented the results from multiple stages of experiments done in the research. Based from parameters optimization experiments, lab-scale experiments have been done. Improvement experiments were performed to overcome the issues from lab-scale production output. There are a few findings that were highlighted in this chapter.

(a) Nanoparticles of Tronoh silica sand have been produced with the size ranges from 41 to 45 nm after 10 hours of milling and heating process combined, with sieving process every two hours of milling.

(b) Although nanoparticles of less than 100 nm have been produced, there are large particles with sizes between 166 to 269 nm as a result of agglomerated particles during milling process. These large particles affect the particle size distribution graph to be bimodal when the desired result is normal or skewed distribution. The large particles are also affecting the median size, d (0.5), span and specific surface area.

(c) Since the large particles are the result of agglomeration during milling process, the problem was reduced by scrapping agglomerated silica sand that are sticked to the inner wall and lid of milling jar. This preventive action is done every 30 minutes of milling. A series of

10 improvement experiments have been done to investigate the effectiveness of the preventive action taken.

(d) The improvement experiments showed a better result compared to the lab-scale production. The median size has been successfully decreased to a size between 44 to 51 nm. Although there are particles larger than 100 nm detected, the size is no higher than 150 nm and is kept to a minimum level.

(e) FESEM analysis justified the findings from particle size analysis as particles lower than 100 nm have been detected. However, the particles are in the shape of cube with sharp edges, far from the desired round shape. Compared to the chemical synthesis of nanoparticles, the shape of particles produced from milling process are harder to control.

(f) EDX analysis showed a significant increase in silica content and purity. The silica content has been increased from 25.77 % weight and 15.84% atomic to 35% weight and 32% atomic. The milling process has proved to increase the silica content while the combination of milling and sieving process managed to increase the purity of silica sand by eliminating impurities such as Carbon which was detected in the raw silica sand.

CHAPTER V

CONCLUSION

5.1 Chapter Overview

This chapter summarizes the works and findings from the research. Recommendations for better results in future researches are also presented.

5.2 Conclusion

The research has established a technique of transforming natural Tronoh silica sand to silica sand nanoparticles by using a combination of low speed ball milling and heating process. By using the optimum parameters identified, silica sand nanoparticles of sizes between 44 to 55 nm have been repeatedly produced. Further analysis using FESEM has confirmed the presence of particles less than 50 nm, while EDX analysis showed that silica sand nanoparticles produced contain high silica purity.

5.3 Recommendations

Despite achieving the research objectives, there are however a few recommendations to improve the result.

(a) Other parameters that should be tested for optimum milling setting is the percentage of milling jar filling. The percentage of milling jar filling is the percentage of silica sand and grinding balls occupancy in the milling jar. Due to limited amount of grinding balls, the highest percentage of filling tested in this research is around 33%. The recommended percentage of filling from previous works and manufacturer is 45% to 55%. Higher percentage of filling provides a better grinding process and reduction of agglomeration.

(b) Using milling jar and grinding balls made from materials with higher hardness can helps to increase the efficiency of milling process. Harder grinding balls materials such as steel can break the silica sand easier and will reduce the milling time as well.

(c) For potential scale-up to mass production, it is recommended that the ball mill machine should be modified to have a built-in heating mechanism. By having a heating feature in the ball mill machine, separate drying process as done in this research can be avoided and results in shorter production time.

5.4 Chapter summary

This chapter has summarized the findings from the research and proved that the objective has been achieved. Recommendations for future works and potential scale-up have been elaborated as well.

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