FINE GRINDING OF SILICA VIA STIRRED MILLING

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LIST OF ABBREVIATIONS

TEA	Triethanolamine
XRD	X-Ray Diffraction
PSA	Particle Size Analyzer
SEM	Scanning Electron Microscope
PSD	Particle Size Distribution
GA	Grinding Additive

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PENGISARAN HALUS SILIKA MENGGUNAKAN MESIN GILING PENGACAU

ABSTRAK

Pengisaran ultrahalus berlaku dalam pelbagai mesin giling bertenaga tinggi, pada kebiasaanya mesin giling bergetar, jet udara dan media kacau. Perubahan struktur dan morfologi dalam zarah kuarza yang dikisar dalam mesin giling pengacau menegak merupakan aspek yang diutamakan dalam kajian ini. Pengisaran menggunakan mesin giling pengacau diakomodasi dengan penambahan bahan aditif pengisaran merupakan langkah yang efektif bagi menghasilkan zarah halus. Matlamat utama adalah untuk menyiasat kesan pelbagai jenis bahan aditif pengisaran, iaitu metanol, triethanolamine, dan sodium oleate, yang digunakan semasa operasi pengisaran terhadap saiz zarah dan analisis bentuk mineral, bagi menentukan dos optimum bahan aditif pengisaran dan parameter operasi jentera yang digunakan untuk menghasilkan produk yang berkualiti terhadap sektor perindustrian. Pelbagai jenis bahan aditif pengisaran dan dos yang berbeza dimasukkan bersama mineral silika selepas ia dirawat tanpa bahan aditif tersebut. Melalui eksperimen ini, bahan aditif pengisaran seperti metanol, triethanolamine (TEA), dan sodium oleate akan digunakan dengan kuantiti dos di antara 0.25 peratus hingga 2.00 peratus, pada julat kelajuan agitator di antara 100 rpm hingga 400 rpm. Ujian pencirian seperti Penganalisis Saiz Zarah (PSA), Alat Pembelauan Sinar X (XRD), dan Mikroskop Elektron Pengimbas (SEM) akan dinilai selepas produk digiling. Kejayaan kerja ini akan membantu dalam penghasilan produk silika dengan taburan zarah yang baik melalui analisis bentuk dan saiz zarah.

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ABSTRACT

The ultrafine grinding occurs in different types of high energy mills, which the most common are vibratory, air-jet and stirred media mills. Stirred media milling is an effective means of grinding into very fine particle sizes is facing high demand from industry but yet has to determine the best practice to enhance the quality of product from fine grinding in term of size and shape distribution. As a result, the best practice as far as the characteristics of the stirred mill to be utilized, as well as the optimum dosage of grinding additives to be used during the grinding operation, will be investigated in this study. The main aim is to investigate the effect of various kind of grinding additives, i.e., methanol, triethanolamine, and sodium oleate, used during grinding operation towards the particle size and shape analysis of mineral, determine the optimum dosage of grinding additives and machinery operational parameters to produce good quality of product for industrial purpose. In this experiment, grinding additives such as methanol, triethanolamine (TEA), and sodium oleate will be used in dosages ranging from 0.25 percent to 2.00 percent, at 100 rpm to 400 rpm in range. Characterization tests such as the Particle Size Analyzer (PSA), X-Ray Diffraction (XRD), and Tabletop Scanning Electron Microscope (SEM) will be evaluated after the product has been discharged from the ceramic jar. The particle size distribution curves display by grinding with addition of TEA and sodium oleate shown highest size reduction to occur, with agitator speed adjusted to the highest level in this experiment (400 rpm). The success of this work will help in producing product of silica with good particle distribution and properties as expected to be shown by particle shape and particle size analysis.

CHAPTER 1

INTRODUCTION

1.1 Background

Stirred media milling is a potential technology for producing colloidal dispersions through wet grinding. Many researchers have previously researched the impacts of various operational parameters in stirred media mills, such as size, shape, type, and quantity of grinding medium, speed of agitator in grinding chamber, feed rate of dispersions, and so on. However, it is still unclear how the concentration of the dispersion influences particle sizing, which generates valuable information about the particle size of the product to interpret, control, and enhance the grinding process during stirred media milling, where particles rapidly change size from micron to colloidal range (Asif Inam et. al, 2011).

The definition of fine grinding differs depending on the application. The fine grinding requirements for the paint and mining industries, for example, are vastly different. Fines are particles finer than 1 micron in the paint business, while fines in minerals processing are particles that are difficult to recover in a separation process. Fine particle size definitions range from below 1 mm to below 10 microns, depending on the kind of separation technique (gravity, flotation, leaching, etc.). The decline of primary minerals deposits has created a need for extracting minerals from complex, finely grained and lower grade ore bodies. These types of ore bodies require fine grinding to liberate the valuable minerals and improved recovery in the flotation or leaching stages (Palaniandy et al., 2015). The need for fine or ultra-fine grinding in concentrators has risen as a result of this occurrence. Stirred milling technique has opened up new possibilities for treating fine-grained ore bodies in the mineral processing sector. Many formerly "untreatable" ore resources have lately been produced thanks to advancements in stirred mill technology, such as at McArthur River Mine and Mount Isa Mine (Burford and Clark, 2007).

Stirred mills are effective grinding equipment for creating micronized materials. Stirred mills have surpassed tumbling mills as the dominant comminution device in fine and ultra-fine grinding circuits and have acquired universal adoption in mineral processing sectors due to their energy sufficiency and liberation benefits. In the process meantime, the attrition breakdown mechanism between the ceramic beads in stirred media mills completely liberates the grinding media particles. Stirred milling is a grinding tool that is used extensively for mineral liberation, in order to achieve successful downstream processing such as flotation or leaching (Reem and Roufail, 2011).

Moreover, the addition of grinding additives as chemical substances gives several advantages such as enhancing grinding efficiency, reducing water usage, improving material flowability, and narrowing the particle size distribution of the grinding products (V. Chipakwe et. al., 2020). The use of grinding additive improves material flowability, which presents an opportunity for the application of dry grinding. This ultimately reduces the environmental impacts such as carbon dioxide emissions due to the energy intensive nature of grinding (J. Jeswiet and Szekeres, 2016). Zheng et al. (1997) tested various types of them in limestone grinding and concluded that the surface area of the product could be doubled with the use of proper grinding aid. Choi et al. (2010) in their stirred mill test works showed that it was possible to reduce the utilized energy by 37% with the use of grinding aids. Within the context of study, 3 types of grinding additives (methanol, triethanolamine and sodium oleate) were tested and the influences on mill performance and product quality were discussed by considering the differences in the agglomeration energies and adsorption mechanisms reported in the final characterization process.

Furthermore, the machinery operational parameters also be tested during grinding process to determine the best practice in order to utilize the optimum stress intensity being held to the grinding media. Among parameters that were studied including the solid concentration of slurry, media filling ratio, grinding time and agitator speed, in which these factors influence the significant process of size reduction in fine grinding. The material to be ground is typically in the form of a slurry, filling the void spaces between the grinding media. The rotation of the stirrer fluidizes the grinding media and creates a radial velocity gradient among them. Particle breakage in stirred mills is caused by rubbing impingement between adjacent media balls, media balls and stirrer, and sometimes, media balls and chamber walls. The grinding time influences the final fineness. For efficient grinding performance, a proper media bead size to material size ratio must be used (Santosh et. al., 2020).

The final purpose of this work is to establish the selection criteria of grinding aids for ultrafine grinding. In this laboratory, the effects of various liquid additives on ultrafine grinding of some minerals have been investigated for several years. In the previous study (M. Hasegawa, Y. Kanda, 1993), the authors reported that alcohols were considerably effective as grinding aids for feldspar although the degree of effectiveness varied somewhat with the species and addition quantities of alcohol. In this paper, the effects of certain grinding additives as well as their optimum dosage were investigated on ultrafine grinding of silica and the stress intensity (agitator speed) on fixed grinding time is studied in this experiment. The results were reported on the behavior of additive molecules during grinding.

1.2 Problem Statement

Stirred media milling is an effective means of grinding into very fine particle sizes is facing high demand from industry. While the process is well established commercially, much remained to be learned regarding the fundamental principles involved and the role of equipment and operating parameters on grinding performance. The industry has yet to determine the best practice to enhance the quality of product from fine grinding especially in term of size and shape distribution which important in quality determination of product. The manufacturing of ultrafine powders is influenced by two counteracting processes which are particle breakage and interparticle interaction (i.e., aggregation and agglomeration). Thus, this study investigates investigate the best practice as parameters of stirred mill to be used, as well as the optimum dosage of grinding additives used during grinding operation in which will enhance the quality of mineral filler in term of particle shape and size.

1.3 Research Objectives

i. To investigate the effect of various kind of grinding additives, i.e., methanol, triethanolamine, and sodium oleate, used during grinding operation towards the particle size and shape analysis of mineral.

ii. To determine the optimum dosage of grinding additives to produce good quality of mineral filler for industrial purpose.

iii. To study the optimum machinery operational parameters, i.e., grinding time, solid concentration and stirrer speed, conducted during milling procedure.

1.4 Scope of Study

This study was carried out to investigate the effect of operational and model parameters on the physical properties of mineral filler through wet grinding using a stirred mill. The experiment begins with the preparation of feed and chemical substances, followed by fine grinding and characterization tests. In this study, a silica sample prepared by Sibelco Sdn. Bhd. with particle sizes less than 75 m was used. Throughout the experiment, several stirred mill operating parameters, such as solid concentration, grinding time, size of media particles, and type of material were remained constant, however the agitator speed were tested at various conditions to determine the optimum stress intensity as to produce good quality product. In addition to that, the media filling ratio, the mass of silica sample, the volume of water used in this experiment all remain constant.

In the other hand, methanol, sodium oleate, triethanolamine (TEA) used as grinding additives in varying amounts ranging from 0.25 wt.% to 2.00 wt.%. As for the agitator speed tested ranging from 100 rpm to 400 rpm, a total of 48 samples were run using stirred milling operation by wet grinding method, according to the Design of Experiment (DOE). The grinding result were characterized by X-Ray Diffraction (XRD), Particle Size Analyzer (PSA) and Tabletop Scanning Electron Microscope (SEM) in order to examine the crystalline structure of particle, particle size distribution and particle shape distribution.

The success towards this research study can increase the production of good quality mineral filler with excellent particle size and shape condition. Thus, the fine grinding process was carried out using a vertical stirred mill with optimal parameters.

1.5 Thesis Outline

The chapter 1 of this research study discussed on the brief description of the research which is providing basic review of the research's background, aims to be achieved, and a quick summary of the scope of study and research's purpose.

In chapter 2, it is a collection review of the literature on research study with detailed discussion of the research focuses on the comminution process in general. A review of previous research on fine grinding methods, particle breaking mechanisms, stirred mill operation parameters, and characterization tests that were applied in this study. The literature covered general and detailed information about comminution and milling procedure as well as particle interaction in grinding operation.

In chapter 3 where the methodology of experimental procedure is discussed, a comprehensive review of the experimental context, including an explanation of the feed and grinding additives preparation, equipment setup, and characterization analysis method to be employed are explained.

Looking forward in chapter 4, analysis data and discussion of experimental results are deliberated. An interpretation of experiment outcomes and data acquired from characterization tests resulted in particle size and shape analysis.

Finally, the conclusion and recommendation are figured in chapter 5 in which all the summarization of research findings and recommendations for future investigations to improve success and accuracy are stated.

CHAPTER 2

LITERATURE REVIEW

2.1 Mineral Filler

Mineral fillers are inorganic finely crushed minerals which designated to improve the quality of materials produced in manufacturing industry. For instance, the criteria to be suited as mineral filler in manufacturing processes are now not only focused on the size of particle but also on the shape of particle, particle size distribution and also the degree of crystallinity of the minerals to manufacture good quality products (Abd. Kadir et al., 2009). Fillers are solid additions that differ in composition and structure from the plastic matrix.

Mineral particle fillers are employed in polymer composites to replace relatively expensive bulk material while also sharing some mineral qualities with the host matrix, hence improving the matrix's properties. Mineral fillers such as talc, mica, wollastonite, and calcium carbonate were loaded into polymers in various forms (K.H. Rao et. al., 1998, Y.W. Leong et. al., 2004, E. Sancaktar & E. Walker, 2004). The mineral filler most widely added to plastic, particularly polypropylene (PP), is calcium carbonate (CaCO3). This filler is inexpensive and can be used at high filler loading (G. Wypych, 2000).

2.1.1 Silica Sand (Quartz)

Silicon dioxide is also known as silica (SiO2). The two most abundant elements in the earth's crust are silicon and oxygen. Sand is a prevalent form of silica in nature. Silica is found in many various forms, both crystalline and non-crystalline (amorphous). Hard, chemically inert, and with a high melting point, crystalline silica is a popular 2material. These are highly prized features in a variety of industrial applications. The most frequent type of crystalline silica is quartz, which is the second most abundant mineral on the planet. It can be found in nearly all types of rocks, including igneous, metamorphic, and sedimentary rocks. Quartz is found in practically all mining activities due to its abundance.

Silica has long been used as a raw material in the glass, mirror, mosaic ceramics, ferro silicon, and silicon carbide for abrasives and sand blasting industries. It is even used as a supporting material in the cast steel, oil and mining, and refractory brick industries. As a bioactive material for bone tissue replacement, silica with calcium additive has developed into a new nanocomposite (Jang H. D., 2008). Silica can also be applied for reinforcing polymer composites in coatings for corrosion protection and plastic bags (Affandi S, 2009) composite polymer gel electrolytes (Walkowiak M. et. al, 2007 and Osinska M., 2009), thermoplastic polymers (Jesionowski T., 2003), and volatile flavor compounds (Dziadas M., 2011).

Silica has simple chemical and crystal structure that is easy to obtain in high purity, crystallises quickly, and has good mechanical qualities. Therefore, SiO2 has been recognized at an early date and has been thoroughly investigated (Juhasz and Opoczky, 1990). In quartz or silica processing, the hard/low density mineral, the breakage rate is very slow at low agitator speed and the specific energy consumption increases linearly with the increase of the agitator speed. Fracture mechanism of the particles is also function of the agitator speed and type of mineral (Reem and Roufail, 2011).

2.2 Grinding Additives

Grinding aid or grinding additives refer to substances which when mixed into the mill contents cause an increase in rate of size reduction (A. Kwade & J. Schwedes, 1997, and A. Kwade, 1999). The grinding additive facilitates size reduction, utilizing less grinding power from the mill without compromising any of the qualities of the resultant cement. Another advantage of modern grinding aids is that they reduce storage compaction. It generally enhances grinding efficiency by lowering the grinding limit during the operation.

A comprehensive study towards the influence of grinding additives on size reduction units is crucial to achieve significant result of particle shape and particle size analysis. The most common organic grinding aids used in the process industry are based on triethanolamine (TEA), triisopropanol amine (TIPA), n-methyl-diisopropanolamine (MDIPA), glycerine, poly-carboxylate ether (PCE), diethyl glycol (DEG) and propylene glycol as shown in Table 1, as in guidelines regarded by R.K. Mishra et. al., (2017). Up to this day, several studies on the effect of grinding additives on efficiency regarding power consumption, grindability, reduction ratio and mill operating parameters such as mill filling have been done (H.S. Chung, et al.,2010; M. Noaparast & A. Rafiei, 2003; P. Prziwara et.al., 2018; K. B. Diler, 2018). Prziwara et al. in 2018 had investigated their effects on bulk properties such as particle size distribution, specific surface area, powder flowability, specific surface energy, and product fineness.

Table 2. 1 Organic grinding aids used in various investigations.

Grinding aid	**Dry or Wet**	**Material**
Methanol	–	Quartz
Triethanol amine (TEA)	Dry	Quartzite

	Dry	Limestone
	Wet	Cassiterite
	Dry	Fly ash
Polyacrylamides (PAM)	Wet	Cassiterite
Triisopropanol amine (TIPA),	Dry	Fly ash
Oleic acid	–	Limestone-Zinc blend
	Wet	Limestone
Steric acid	–	Limestone
Sodium Oleate	–	Quartz
	Wet	Limestone
Caprylic acid	Dry	Chrome-ore
Marine oil	Dry	Chrome-ore
Polyacrylic acid (PAA)	Wet	Calcite
	Wet	Limestone
	Dry	Gypsum ore
Citric acid	Wet	Hematite ore
Sodium sulphonapthenate	Wet	Quartzite
Heptanoic acid (HepAc)	Dry	Limestone
Amyl-acetate	–	Quartz
Acetone	Dry	Cement clinker
Aryl-alkyl sulphonic acid (RDA)	–	Graphite

2.2.1 Methanol

Methanol is the primary alcohol that is the simplest aliphatic alcohol, comprising a methyl and an alcohol group. It is an alkyl alcohol, a one-carbon compound, a volatile organic compound, and a primary alcohol. With the chemical formula of CH_3OH or CH_4O, it has a molar mass of 32.04 g mol^{-1} and a density of 0.792 g/cm^3.

2.2.2 Triethanolamine

Triethanolamine (TEA) is a polar organic compound with an amine and hydroxyl groups often used as a grinding activator especially for the cement clinker due to strong adsorption onto the surface of particles (Toraman et. al., 2016). It can be bonded to the surface via hydroxyl groups, i.e., alkoxylation on the surface via covalent bonds or in the presence of acid by bonding the ammonium cation to the surface anions via ionic bonds. Zhao et al. (2015) demonstrated that in the cement clinker grinding, the free electron pair of the TEA amine group ensures high electronegativity. Hence strong electrostatic repulsions are present, the material is strongly dispersed so smaller paticles are obtained during grinding.

The presence of TEA lead to decrease in size of agglomerates, which was proved in the work by (Prziwara et al., 2018). The TEA efficiency also varies with different type of mills and duration of grinding. Allahverdi and Babasafari (2014) found out that in clinker grinding with 0.6% of TEA, the ball mill is more effective to the product fineness than vibration mill even though the ball milling is longer, which, however, ensures enough time for effective distribution of TEA. From the mentioned concise overview, we can see TEA is a widely used dispersant in dry grinding.

2.2.3 Sodium Oleate

Sodium oleate is the sodium salt of oleic acid, a monounsaturated fatty acid. The sodium "salt" of oleic acid, Sodium Oleate ($NaC_{18}H_{33}O_2$), is an organic additive. It comes in the form of a powder of small yellowish crystals that dissolve in water and alcohol. In mining industry, it is often used as floating agent in the flotation mineral processing and grinding aid as in grinding and milling operation, however in non-mining sector, it has variety of uses. In cosmetics, sodium oleate is used for its cleansing, thickening and gelling properties. Sodium oleate is used in soaps and detergents as an emulsifying agent. It is also used in the coating of waterproof fabrics. Sodium oleate is also used in the manufacture of industrial lubricants.

2.3 Ultra-fine Grinding

Fine particulate matter has a wide field of application in many industries including paint and lacquer, ink, pharmaceutical, electronics, agro-chemical, metallurgy and ceramic, coal and energy to mention just a few (Conley, 1983; Stanley et. al., 1973). Though the mechanisms of fine grinding are still far from being clear, significant achievements have been made in this direction in recent years (Bernotat S. and Schonert K., 1988). The theory of future mechanics has been proposed and used by a number of researchers to explain the breakage of particles when subjected to compressive forces. These forces lead to the development of both intense compressive and tensile stresses which result in brittle fracture. On the other hand, if the stress is concentrated within a small volume and with fewer flaws, the tensile stress produces shearing (Rumph, 1973). The implication is that as particles get smaller in size, there is tendency towards plastic deformation irrespective of the type of material. According to (Kendall, 1978) it was