SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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FABRICATION OF PORCELAIN GRINDING MEDIA MADE OF LOCALLY PROCESSED CLAY

by:

FAIRUZ BINTI HAMISAN

Supervisor: Dr. Shah Rizal Bin Kasim

Co-supervisor: Prof. Dr. Zainal Arifin Bin Ahmad

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Fabrication of Porcelain Grinding Media Made of Locally Processed Clay**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar tittle of this for any other examining body or university.

Name of Student	: Fairuz Binti Hamisan	Signature:
Date	: 4th July 2017	

Witness by

Supervisor	: Dr. Shah Rizal Bin Kasim	Signature:
Date	: 4th July 2017	

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LIST OF SYMBOLS

~	Approximately
µm	Micronmeter
λ	Wavelength
°C	Degree Celcius
°	Degree
Å	Angstrom
d_i	Diameter of dry sample
d_f	Diameter of fired sample
wt%	Weight percentage
W_D	Dry weight
W_I	Immersed weight
W_S	Soaked weight

LIST OF ABBREVIATIONS

F	Potash feldspar
FESEM	Field Emission Scanning Electron Microscope
GPa	Giga Pascal
ICDD	International Centre for Diffraction Data
K	Kaolin
L	Locally processed clay
MPa	Mega Pascal
POP	Plaster of paris
RM	Ringgit Malaysia
rpm	Rotation per minute
Q	Quartz
VHN	Vickers hardness number
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescene

FABRIKASI DAN PENCIRIAN MEDIA PENGISARAN PORSELIN MENGGUNAKAN LEMPUNG TERPROSES TEMPATAN

ABSTRAK

Kajian yang dijalankan ini adalah bertujuan untuk menghasilkan bebola seramik sebagai media pengisar pada suhu pembakaran rendah yang mempunyai sifat-sifat mekanikal dan fizikal yang unggul berbanding media pengisar sama yang didapati secara komersial. Dalam kajian ini, lempung terproses tempatan dari Trong (Taiping, Perak) telah digunakan sebagai bahan mentah utama untuk menghasilkan media pengisaran porselin dengan penambahan kaolin, kalium feldspar dan kuarza. Objektif kajian untuk menghasilkan media pengisaran porselin menggunakan lempung tempatan diproses dengan komposisi dan suhu bakar berbeza. Lima komposisi bahan mentah yang berbeza (CB1, CB2, CB3, CB4 and CB5) disediakan. Kelikatan slip diukur dengan meter likat. Kaedah tuangan slip telah digunakan sebagai teknik pembentukan. Selepas tuangan, produk tuangan dikeringkan pada 90°C selama dua hari sebelum dibakar pada tiga suhu berbeza (1150°C,1200°C,1250°C) selama 1 jam tempoh rendaman (kadar pemanasan dan penyejukan 5°C/min). Produk yang telah dibakar dicirikan dengan pemerhatian fizikal, pengukuran pengecutan, ketumpatan pukal dan pengukuran keliangan menggunakan prinsip Archimedes dan prestasi media pengisaran akan dinilai melalui proses pengisaran terhadap pasir silika (saiz partikel: 1000 μm) selama 4 jam. Secara keseluruhan, sampel CB1 yang dibakar pada 1250°C menunjukan pengecutan (9.94%) dengan ketumpatan pukal tertinggi (2.31g/cm^3), keliangan ketara terendah (4.79%) dan tinggi kekerasan (5.6GPa). Ini disebabkan pembentukan fasa kekaca. Sampel CB1 juga menghasilkan partikel pasir silika

paling halus (6.85 µm) setelah proses pengisaran. Ini disebabkan ketumpatan tertinggi media pengisaran porselin (2.31g/cm^3) yang memberikan daya hentaman yang berkesan ketika proses pengisaran. Oleh itu, kajian ini telah membuktikan bahawa lenpung terproses tempatan berkebolehan untuk fabrikasi media pengisaran porselin.

FABRICATION AND CHARACTERIZATION OF PORCELAIN GRINDING MEDIA MADE OF LOCALLY PROCCESSED CLAY

ABSTRACT

The aim of this research is to fabricate locally processed clay produced low firing temperature porcelain balls as grinding media with superior mechanical and physical properties than the similar commercially available grinding media. In this study, locally processed clay from Trong (Taiping, Perak) was used as main raw material to make the porcelain grinding media by addition with kaolin, potash feldspar and quartz. The objectives of this study were to fabricate porcelain grinding media by utilizing locally processed clay with different composition and firing temperature. Five different raw material compositions (CB1, CB2, CB3, CB4 and CB5) were prepared. The slip viscosity was measured by viscometer. Slip casting was used as shaping technique. After the casting process, the casted product were dried at 90°C for two days before firing at three different firing temperature (1150°C,1200°C,1250°C) with 1 hour soaking time (5°C/min heating and cooling rate). Fired products were characterized with physical observation, shrinkage measurement, bulk density and porosity measurement by Archimedes principle and the performance of grinding media will evaluate via milling silica sand (particle size: 1000 µm) for 4 hours. Overall, CB1 samples fired at 1250°C have shown the highest shrinkage (9.94%) with high bulk density (2.31g/cm^3), lowest apparent porosity (4.79%) and higher hardeness (5.6 GPa). This is because formation of glassy phase. CB1 samples also produce the finest particle of silica sand (6.85 µm) after the milling process. This is due to the highest density of the fired porcelain grinding media (2.31g/cm^3) which give the effective

impact force during the milling process. Therefore, this research proved that has potential to fabricate porcelain grinding media.

CHAPTER 1

INTRODUCTION

1.1 Research background

Comminution is a process of reduction of particle size of rock by breaking crushing or grinding required to beneficiation process (Sheldon, 2014). Comminution needed huge consumer energy, and is a suitable target for significant savings (National Research Council (U.S.), 1981). High level of energy consumption is needed to obtain finer grinding that essential by fine grained ores demands (Sheldon, 2014). In grinding process, the energy consumption can be reduced by controlling the grinding media.

Grinding process is a final stage in comminution where the particles are reduced in size by a combination of impact and abrasion, either dry or in suspension in water (Wills, 2006). The type of grinding machine that usually used in mineral industry was tumbling mill. These mills exist in a variety of kinds such as ball, rod, pebble, autogeneous and semi-autogenous (Gupta, 1993).

Milling produces a particulate particle size distribution and deagglomeration of fine powders. Physical processes include impact, shear between two surfaces and crushing by a normal force between two hard surfaces. Usually, milling process is used for petroleum products, printing ink, powders for the detergent industry, cosmetics and food processing (Austin, 1984). Milling consume high cost in grinding circuit operators (Moema and Papo, 2009). Usually, grinding of mineral is made of metals and non-metals and in the formed of ball shape or rod mills (Aldrich, 2013).

Metals balls grinding media commonly used are steel, stainless steel, carbon steel, and chrome steel. Next, non-metals balls usually used are made of ceramic materials such as silicon carbide, silicon nitride, zirconium oxide, alumina and porcelain. The ball shape of grinding media was higher consumable costs which is approximately 40% to 45% (Moema, 2009). Therefore, in order to reduce the consumable cost of media, superior physical properties of media was choosen.

Steel based grinding media balls are commonly used in mineral processing industry for reduces ore mineral particles and others industry. Steel balls are suitable for milling hard ores such as gold and coal because it has excessive impact toughness and rough grinding (Aldrich, 2013). Thus, steel balls very suitable and recommended to milling materials wherever high wear, large impact and rough grinding is required. However, during mechanical milling such as wet grinding there is possibilities for contamination of iron (Fe) occurred. Milling with a liquid surface agent can lower particles' surface energy, allowing smaller particle size develop. But, some becomes absorbed into the samples as a contaminant (David, 1949). So, steel balls have been circumscribed in the production of sensitive products such as food processing.

Non-metals balls regularly used are made of ceramic materials such as silicon carbide (SiC), zirconia (ZrO_2), alumina (Al_2O_3) and porcelain (Kotze, 2012). Ceramic balls are often an excellent choice for fine and ultra-fine grinding when a high purity product is required. Furthermore, ceramic balls typically used in applications where contamination from ferrous media cannot be tolerated for esthetics reasons, or where iron in a downstream extraction process inhibits recovery. Their extremely high hardness and complete resistance to most corrosive slurries provide for long service life in abrasive and chemically hostile environments (Gao, 2008).

Porcelain manufacturing has received great attention due to cheap raw materials and simple processing equipment (Iqbal, 2008). Porcelain is broadly used in dinnerware, sanitary ware, medicine and cosmetics. In addition, porcelain are also greatly been used as grinding media (Yahya, 2016). Porcelain has excellent properties such as low water absorption (<0.5%), high mechanical strength (>35MPa) and excellent chemical resistance (Martín-Márquez, 2008). All properties stated above, produce good porcelain ball which is suitable to mill and mix coarse particles in order to produce fine powders. Porcelain ball are ceramic balls that function to prevent any occurrence of contamination during food processing because it can prevent chemical reaction between porcelain grinding media and food.

In general, porcelain are mainly composed of clay (kaolinite, $[Al_2SiO_2O(OH)_2]$), flux and filler. There are two different types of clays that available in Malaysia which is ball clay and kaolin (Harun, 2015). In this study, locally processed clay from Trong, Taiping (Perak) was selected to observed their potential application as grinding media. Yahya (2016), has reported that locally processed clay from Trong has good physical and mechanical properties which are it has high hardness (7.32 GPa) and compressive strength (381.6 MPa) that has superior properties thanthe commercially available porcelain balls. The clay content gives shaping abilities to the body which aids to provide plasticity for the body to shape and form into desired shape (Valášková, 2015). Potash feldspars as a fluxing material react with other materials upon firing and form enough glass phase or liquid at commercial firing temperature (~1200 to 1300^{o}C). Therefore, densification on the body is occurred when the gaps and voids in the microstructure are filling up with the liquid (Iqbal, 2008). The filler such as quartz reduce the tendency of distortion and shrinkage of the body and improve the mechanical properties (Martín-Márquez, 2008).

There are several techniques used to fabricate porcelain ball such as isostatic press (Yahya, 2016), rolling and casting (Aiyar et al., 1994). In this study, slip casting method was implemented to produce porcelain balls. Slip casting process can produces high green densities and micro structural homogeneity, even complex geometries by mixing ceramic powder and water (slip) that poured into porous mould. It is simplest methods reproducing ceramic objects and advantage of permitting the making of a large number of exact replicas of an original model (Evcin, 2011). Hence, it can be suggested that this process capable to produce large amount of porcelain balls at one time.

From this study, the potential of local clay in the fabrication of porcelain balls via slip casting method might open huge opportunities to manufactures the porcelain balls as grinding media with lower cost and good quality.

1.2 Problem Statement

Significant reduction in liberation size of mineral deposits, processing cost and grinding media contamination in worldwide has challenged the minerals industry to come up with efficient technologies to reduce enormous energy required for fine grinding and to achieve economically processing in grinding process (Moema, 2009).

Ball milling process was most favorable grinding methods that are using ball as a media in many industries such as brewing industry, chemical, mineral preparation, laboratory milling, charcoal for briquetting, cosmetics and food processing (Austin, 1984). According to Massola (2016), almost 53% of the grinding applications in the world use balls mills and about 90% of mining activities are users of balls as grinding media. The ball mill grinding media need to be strong and tough material enough to grind materials such as steel ball. Steel balls suitable to grind hard ores to reduce particle size (Aldrich, 2013). However, steels balls will cause contamination because of long time used or during wet grinding the iron (Fe) absorb into product. Therefore, steel balls is not suitable for grinding sensitive product such as in food processing.

Another examples is reducing the particle size of food to achieve homogenization (Nielsen, 2003). Ceramic balls are used to grind frozen foods without predrying and also reduces undesirable heat-initiated chemical reactions occuring during milling (Pomeranz, 1994). Therefore, steel balls are not suitable to grind food because of heat transfer between food and ball can gives chemical reaction and produce contamination.

Porcelain balls can be produced using locally processed clay material and fabricate by using slip casting process to reducing consumable cost and contamination. According to Yahya (2016), it has reported that Malaysia has a quality source of raw materials such as kaolin that capable to produce porcelain balls. Ginung (2015), has stated Malaysia has produced 219,652 tonnes kaolin or kaolinitic clay in 2014 which cost RM15.8 million.

Porcelain grinding media with high green densities and microstructural homogeneity can be produce by slip casting method (Ferreira et al., 2003). Further more, slip casting method is a inexpensive process that can produce large amount of porcelain balls compared to hand making that needed more workers energy (Evcin, 2011; Razak et al., 2014).

Yahya (2016), has stated utilize the potential of locally processed clay in making porcelain balls grinding media is very important because not many studies done on the potential of local clay.

1.3 Research Objectives

The research objectives of the study are as follows:

i. To utilize the potential of locally processed clay in making porcelain balls grinding media.

ii. To analyse the effect of sintering temperature and composition on the properties of porcelain grinding media produced.

1.4 Research Scope

In this study, to achieve the mentioned objectives, this research work divided into three main stages which are the characterization of raw materials, slip and fired porcelain grinding media.

Four different raw materials were used to produce porcelain ball which is locally processed clay (L), kaolin (K), potash feldspar (F) and quartz (Q). The raw materials were characterized for phase analysis, chemical composition, morphology and particle size analysis. X-Ray Diffraction (XRD), X-Ray Flourescene (XRF), Field Emission Scanning Electron Microscope (FESEM) were used to investigate the mineralogical phases, chemical composition and morphology.

Next, sample preparations including making working mould and slip. The porcelain ball of grinding media was produce via slip casting. In this study, working mould has been prepared by using Plaster of Paris (POP) and a commercial steel ball as model. The weight percentage (wt%) ratio between POP and water is used for this work is 60:40.

The grinding media that required being prepared contained five different compositions. The porcelain ball fired at three different firing temperatures (1150^{o}C, 1200^{o}C and 1250^{o}C) for each composition with 1 hour soaking time and 5^{o}C/min of heating and cooling rate.

Lastly, the fired samples were tested with various testing that involve the physical appearance, shrinkage measurement, bulk density and porosity testing by Archimedes principle and the hardness of porcelain balls. The performance of grinding media been analyze by milling silica sand for 4 hours.

CHAPTER 2

LITERATURE REVIEW

2.1 Ceramic

Ceramics can be defined as a solid heat resistant, non-metal and inorganic generally consists of compounds formed from elements of metal and non-metal. Ceramic gets its name from the word keramos Greek, means "pottery", which in turn is derived from the Sanskrit root that older, means "to burn". The Greeks used the term means "burnt stuff" or "burned earth". The old term has been including all products made of clay fired, for example bricks, fireclay refractories, sanitary ware and tableware (Carter, 2007). In general, ceramic is a hard and brittle material. Ceramic materials are divided into three categories of traditional ceramics, engineering ceramics and glasses (Smith, 2006). The white wares were consisting of table or decorative ware, wall tiles and sanitary wares as products from ceramic (Ryan, 1987).

A ceramic material or product defined as one composed of inorganic but non-metallic material. On this basic, ceramic products are usually can be divided into four categories with as their structural products such as bricks, roofing tiles, pipes or floor tiles (Ryan, 1987).

2.1.1 Traditional Ceramics

Three basic components in traditional ceramic are made up of clay, silica or stone of fire and feldspar (Kamseu, 2007). Traditional ceramics are usually based on clay and silica (Carter, 2007). Clay in traditional ceramic material as workability before it shots and provides harden and it is the main body material (Smith, 2006).

Traditional ceramic consists of at least three components for optimum processing, and hence the performance of the final products such as kaolin or kaolinite clay for plasticity, feldspar for fluxing and silica as filler for the structure. Composition triaxial porcelain has a composition (SiO_2. Al_2O_3. KNaO). Sodium feldspar for soft porcelain has 25 wt% of plastic component, 25 wt% silica and 50 wt% feldspar of sodium feldspar (Kamseu, 2007). Hard porcelain has 50 wt% of clay, 25 wt% silica and 25 wt% feldspar of potassium feldspar (Kamseu, 2007).

Traditional ceramics refers to ceramic which are produced from unrefined clay and combinations of refined clay and powdered or granulated non-plastic minerals. Clay content of traditional ceramics are used around exceeds 20% (Lee, 1961). The general classifications of traditional ceramics are as described in Table 2.1.

Table 2.1: The general classification of traditional ceramics (Groover, 2010)

Classifications	Descriptions
Pottery	Used as a generic term for ceramics that contains clay and is not used for structural, technical or refractory purposes.
White ware	Ceramic ware that is white, ivory or light gray in colour after firing. White ware is further classified as earthenware, stone ware, china ware, porcelain and technical ceramics.
Earthenware	Glazed or unglazed non vitreous (porous) clay based ceramic ware. Applications include kitchenware, ovenware, table ware and tile.
Stoneware	Vitreous or semi vitreous ceramic ware of fine texture, made primarily from non-refractory fire clay or some combination of clays, fluxes and silica that when fired has property similar to stone ware made from fireclay. Applications include chemical ware, cook ware, drainpipe, kitchenware, table ware and tile.
China ware	Vitreous or ceramic ware of zero or low absorption after firing that is used for non-technical applications. Applications include artware, ovenware, sanitary ware and tableware.
Porcelain	Glazed or unglazed vitreous ceramics ware used primarily for technical purposes. Applications include artware, ball mill balls. Chemical ware, insulators and table ware.
Technical ceramics	Vitreous ceramics whiteware used for such products as electrical insulation or for chemical, mechanical, structural or thermal applications.

2.2 Grinding Mill

Size reduction or comminution of solids by crushers and mills is a very significant operation involving many aspects of powder technology. Size reduction is a process of reducing large lumps unit masses into small masses, coarse particles or fine particles (Abouzeld, 1994).

Grinding is the last stage in the process of comminution which in this stage the particles are make smaller in size by a mix of abrasion and impact, either dry or wet (Wills, 2006). A material must be reduced from lumps of op to a meter in size to a fine powder, sometimes a powder essentially less than 100 μm in size. Size reduction over many orders of magnitude in size cannot be efficiently achieved in a single machine and a sequence of different types of machine is used, each machine designed for efficient operation on a particular feed size.

2.2.1 Types of grinding mill

In recent years, the demand for better fine-grinding mills had become apparent due to new processes and products in minerals, chemical and ceramic industries (Yahya, 2016). They are various milling machine have been used to produced finer particles which are tumbling, attritor and vibratory.

2.2.1.1 Tumbling grinding mill

Tumbling ball mill is the most famous grinding mills which are contain a rotating cylindrical tank with grinding media such as balls. The tumbling ball mill is broadly used in thermal power plant, cement and mineral industries. In mineral industry, tumbling mills was used to grind coarse particles (5 to 250 mm) to finer particles (40 to 300 μm) (Wills, 2006). The tumbling mill, as the most crucial mechanical installation in the pulverizing system, use a large amount of energy electricity, approximately 65 to 75% of the energy used by the pulverizing system and 15 to 20% of the energy used by the entire power plant

(Si et al., 2009). The grinding performance is connected to the ball movement in a drum during milling and is reliant on operational conditions such as balls filling in the drum, rotational speed, mill size and sample charge. Mainly, in wet milling, viscosity and solid concentration of slurry in a jar are important parameters to determine the optimum circumstances.

Tumbling mill is consisting of a horizontal rotating cylinder that filled up with 40% by volume with grinding media. Owing to the spinning the grinding media are raised and get potential energy which will be moved into kinetic energy in cascading and/or cataracting manner in Figure 2.1 (McKeen, 2006). Cascading is determined by contact mechanics, where grinding activity takes place via collision and attrition (Deniz, 2013). Collision is impact among particles, media and the milling tool and meanwhile, attrition is mass loss at the surface of spherical media by other particles glide over them or they glide over the liner mill (Nawaz et al., 2010;Cleary and Morrison, 2016).

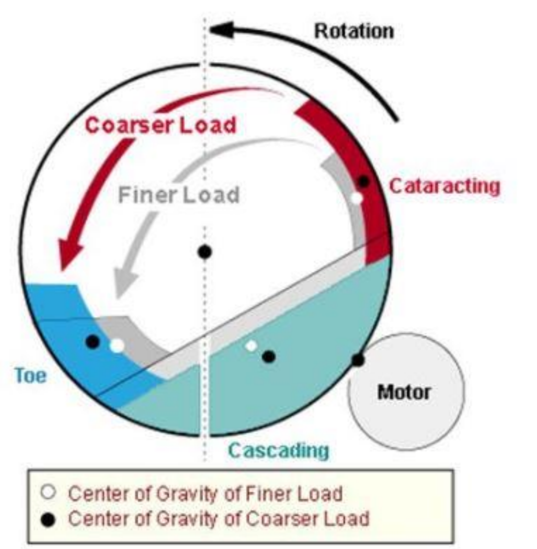

Figure 2.1: Cascading and cataracting action in tumbling mill (Mckeen, 2006)

Cascading is an occurrence where the grinding media from the outside falls and rolls in a consistent, mobile mass as indicated is a waterfall. The impact breaks the grains or the charge. The feed material to be ground is scattered in the grinding media and emphasized by pressure and abrasion between layers of media or by impact of falling balls. When a mill is spun too faster, the grinding media and mill base are forced to the exterior of the mill by centrifugal force as shown in Figure 2.2. No milling occurs at all in this situation. Lowering the rotational speed slightly generates what is called action, which is large impact while grinding is much less effective (McKeen, 2006).

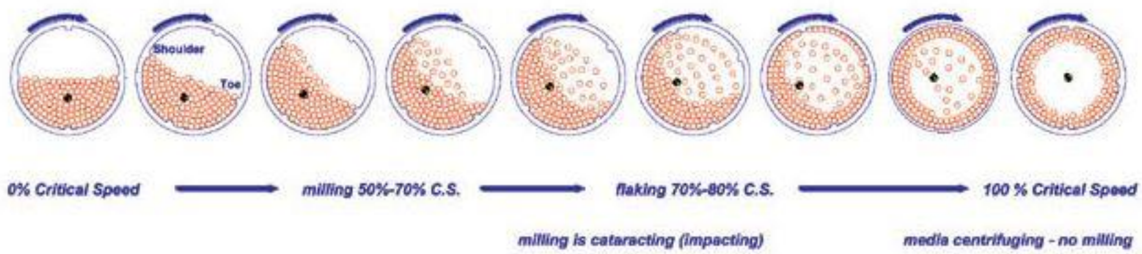

Figure 2.2: Schematic diagram possible operating regime of a tumbling mill (McKeen, 2006)

A tumbling mill is most extensively applied in both dry and wet methods, in batch and sustained operations, and on small and large scales. The most favourable rotational speed is commonly set as 70 to 80% of critical speed, N_c (rpm) (Deniz, 2013). Critical speed is minimum speed at which the tumbling media is held against the shell by the centrifugal ^{force}. The balls are stick to the wall as a result of centrifugation as Equation 2.1

$$N_c = \frac{42.3}{\sqrt{D_m - d_b}} \qquad \text{Eq. (2.1)}$$

where D_m and d_b are the mill diameter and the ball diameter in metres, respectively. It is desirable to decrease the ball size corresponding to the smaller size of supplied materials (Kanda and Kotake, 2007).

The most common types of tumbling mills are the ball, rod, autogenous and semi-autogenous mills (Radziszewski et al., 2005). Figure 2.3 shows schematic of a tumbling ball mill which used a ball as grinding media (Lynch and Rowland, 2005). Ball mill is commonly used in mineral industry as fine grinder type such as reduction of Portland cement. Ball mill is in the form of a horizontal rotating cylinder is crush materials to the needed fineness by impact and abrasion with the media balls which partly topped up with balls, normally metal, stone, or ceramic. Normally, about 30% times the diameter and distinguished by their longer length and smaller diameter. The feed of starting material is at one end of the cylinder and the discharge at the other side.

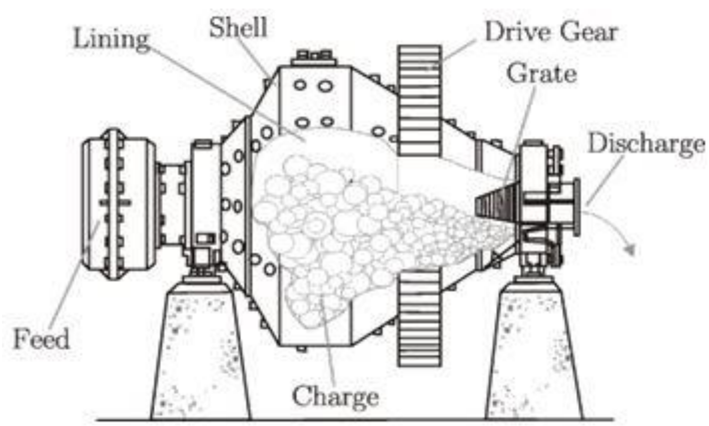

Figure 2.3: Schematic of a tumbling ball mill (Lynch and Rowland, 2005)

Rod mill is a rotating tank causes attrition and abrasion between ore particles and steel rods as shown in Figure 2.4 (Vermeulen et al., 1984). Rod mills are less familiar compared to ball mills for minerals processing. Rods used in milling are usually the type of high carbon steel which differs in both the length and diameter. Grinding is more efficient to use a smaller rod due to increase the total surface area. Autogenous mills are self-grinding of the ore which does not use media balls. The compressive grinding of finer particles and impact breakage of bigger rocks caused by rotating tank hurls bigger rocks of ore in a cascading movement. Semi-autogenous (SAG) mill are basically autogenous mill, but used media balls to assist in grinding similar in a ball mill. A SAG mill is commonly used as a main or first stage grinding resolution which uses a ball charges between 8 to 21% (Radziszewski et al., 2005).

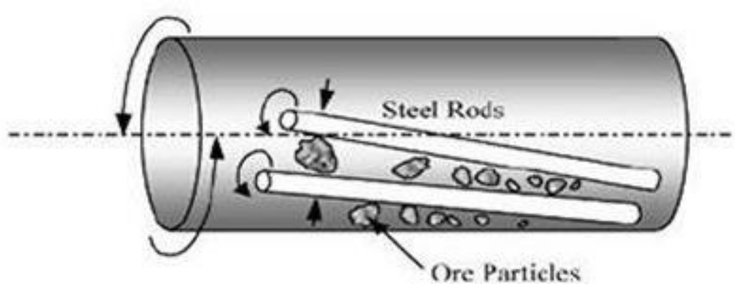

Figure 2.4: Schematic of a rod mill (Vermeulan et al., 1984)

Depending on the type of ore, there are different charge media to be used. In rod and ball mills, the different charge media are usually made of steel and added to the mill. In autogenous mills, the ore itself is used as charge medium. Generally, a pebble mill is used as secondary stage in autogenous grinding and then the pebbles are taken from the first process step, the autogenous mill. Alternatively, the pebbles may consist of screened out lumps of gangue if there is a lack of pebbles.

2.2.1.2 Attritor grinding mill

Attrition grinding mill as shown in Figure 2.5 was introduced to the industry in 1922. This grinding mill is containing internally agitated media. The attritor is one of the most efficient fine grinding and dispersing or comminuting pieces of equipment available today for the fine grinding of ceramic materials.

A key to the efficiency of attritor ball mill grinding is that the power input is used directly for agitating media for grinding and is not used for rotating or vibrating a large, heavy vessel in addition to the media charge.

Furthermore, attrition mill is used for quickly to obtain fine sulphur diffusion for use in the rubber vulcanization process (El-Eskandarany, 2001). Furthermore, this mill also called Szigvari attritor grinding mill. In this mill, the stirring movement of an agitator which has a perpendicular rotating central shaft with horizontal arms of the grinding process occurs. Normally, the rotation speed of central shaft is about 250 rpm.

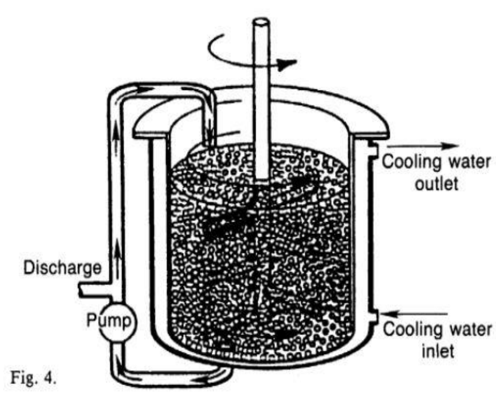

Figure 2.5: Attritor ball mill (El-Eskandarany, 2001)

The equation 2.2 can be used to relate grinding time to media diameter and agitator speed:

$$T = \frac{KD^2}{\sqrt{N}} \qquad \text{Eq. (2.2)}$$

With,

T : grinding time to reach a certain median particle size

K : a constant that varies depending on material being processed, type of media, and the model of attritor being used

D : media diameter

N : shaft rpm

This equation shows that the total grinding time is directly proportional to the media, or ball diameter, and inversely proportional to the square root of the shaft rpm. This equation also shows that increasing the media size increases the grinding time, but decreasing the media size decreases grinding time (John, 2009).

2.2.1.3 Vibratory mill

Vibratory mill are commonly used in high energy ball mill to prepare ceramic materials. The vibratory mills are smaller compared to other mills which about 10 ml in volume. The drum vibratory mill which including the powder and media is strongly vibrated. The impacts between the media are much more aggressive than they are in ball milling. This can reduce milling times and also produce nanopowders (Carter and Norton, 2013). Polymer balls can be used as media to prevent any contamination because it can be burned off during following firing. In this mill, the milling tools and charge of the powder are vibrated Figure 2.6 at extremely high speed, as high as 1200 rpm (El-Eskandarany, 2001).

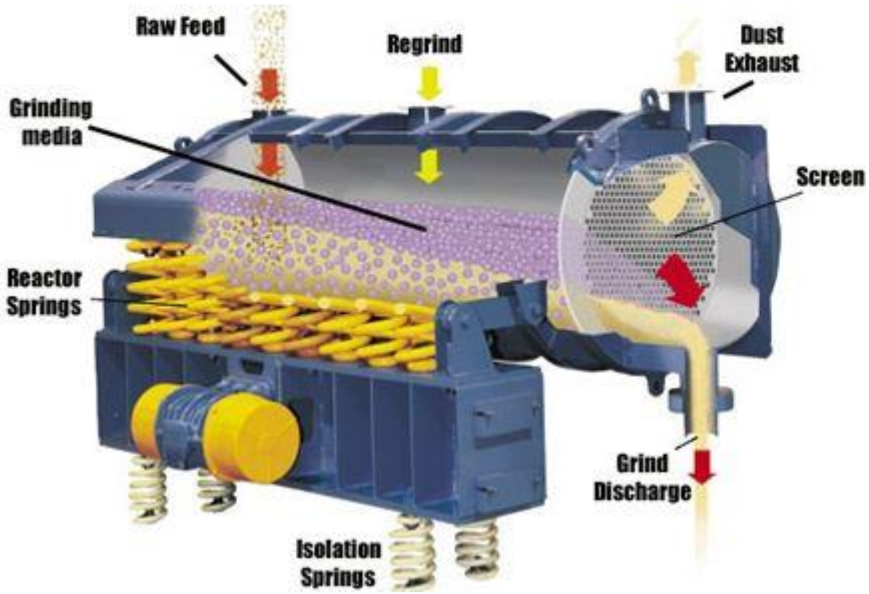

Figure 2.6: Diagrammatic view of the vibratory ball mill (Gock and Kurrer, 1999)

In vibratory mills, the grinding media receives rapid impulses at a rate proportional to the vibrational frequency of the mill. Impact forces acting on the powder exceed shearing and friction forces. Vibratory mills utilize smaller grinding media because of higher impact forces, frequencies and acceleration.

The rate of processing in a vibratory mill is proportional to the diameter of the balls and their density, proportional to the cube of the frequency of vibration, while not significantly affected by chamber diameter. The rate of processing increase as the amount of powder in the mill decreases and is greater with balls than other shapes, but rods provide the more homogenous product.

2.3 Grinding media

Grinding media have a significant effect on the performance of milling process in terms of energy consumption, product size distribution and grinding costs (Wills 2006). Grinding media costs compared with overall grinding costs are usually high and need to be minimized. As a consequence, many surveys have been conducted to study the effect of different shape of grinding media on the grinding process. They found that spherical balls or spheres were more efficient than other grinding media shapes (Simba and Moys, 2014; Lameck et al., 2006). Grinding mill usually uses some shape of media such as spherical, cylinder or cylpebs, and eclipsoids as at Figure 2.7. Eclipsoids are semi-prolate spheroid (stretched ellipsoid of revolution). Their shape is similar to that of a half rugby ball football. At present, the spherical ball as grinding media has been the choice over than forms of grinding media due to efficiency of milling process (Simba and Moys, 2014).

(a) (b) (c)

Figure 2.7: Shape of grinding media used for milling process such as (a) spherical, (b) cylinder and (c) eclipsoids

Grinding media form a significant part of the operating costs of the mill operation. As the grinding proceeds, the grinding media become worn or break. As a result, fresh grinding media must be added in the mill. To reduce grinding media consumption, several approaches were proposed: the use of higher-quality, wear-resistant grinding media and use of cheaper grinding media (Chen et al., 2006; Aldrich, 2013; Breitung-Faes and Kwade, 2008). Two types of grinding media balls in the market are metals and non-metals (Aldrich, 2013). Metal balls are made from steel and non-metal balls are made from ceramic materials such as tungsten carbide, aluminium oxide and porcelain.

2.3.1 Metal balls

Meanwhile ball mill was discovered, it has become a most popular and non-replaceable grinding methods in many industries such as ceramic, steel, glass, cement, cosmetics manufacturers and food processing. During initial the initial years of ball mill utilization, white cast iron balls and flint pebbles were the most common grinding media (Weiss, 1985). The competition was resolved in favour of the white cast iron balls, which grave greater grinding capacity because of their higher specific gravity. The balls were also able to grind coarser feed material and had in most cases a lower cost per ton of ore milled. Pebbles remained preferable in cases where iron contamination was a problem.

Forged carbon steel balls and cast or forged austenitic manganese steel balls were also available, but their application was restricted to high impact conditions only that would have otherwise spalled or broke white iron balls. Widespread use of these balls was limited by the high production costs. The utilization of the austenitic manganese steel balls appears to have been discontinued by the mid 1930s probably because of their high alloy content and somewhat disappointing abrasion resistance compared to the high carbon steel balls (Weiss, 1985). Meanwhile, the development of automatic high speed ball forging machines in the early 1930s, lowered the production costs of forged balls making them, in some cases, economically competitive with white iron balls in low impact mills. The addition of alloying elements and hardening heat treatments developed in the late 10930s further enhanced the competitive position of the forged steel balls.

The exploitation of low grade ores during World War II, 1939 led to the development of metal mould casting machines aimed at producing low cost balls. The resulting products had many imperfections such as large shrinkage and gas cavities, shifts and offsets and projecting sprues. The low production costs and low-impact mills operated at that time. The later development of larger, higher impact mills and a general demand for better quality diminished the use of these white cast iron balls. The late 1940s saw the development of low alloy steel balls. New casting techniques ensured sound shrinkage-free balls (Weiss, 1985).

After 1945, nickel and chromium became more available. The small sizes were popular in cement mills where they were used to achieve the fine grinding that was required. The end of the war also saw the commercial development and use of, first the high chromium and then the chromium-molybdenum martensitic white iron balls. These two ball types are still in production today. The high chromium-molybdenum grades, which were developed around 1960, were found to have abrasion resistance three to seven times, that of forged steel balls when used in cement grinding (Weiss, 1985). These grades have displaced most of the low alloy steel balls, and today are still used for milling cement and other soft materials as well as in highly corrosive milling environments (Weiss, 1985).

Grinding balls are generally made of rolled high-carbon or forged or ally steel and consumption depending on fineness of grind hardness of ore and wear characteristics of the media (Madlool et al., 2011). With respect to grinding media, worldwide steel consumption alone is estimated at more than 600 000 tonnes per annum (Lianyun et al., 2005). The consumption of steel ball can be very high amount, sometimes as much a 40% of the total milling cost, therefore is a sector that often needs special consideration (Wills, 2006). The grinding media may be more expansive due to high quality, but might be economic because of lower wear rates. There are few types of steel ball as grinding media in the market such as stainless steel, forged carbon steel, carbon steel and chrome steel as shown in Figure 2.8. Forged carbon steel normally used low-carbon alloy, high manganese steel, high manganese alloy steel and high carbon steel. Chrome steel ball is expansive compared to other steel ball and can reduce iron contamination during grinding (Peng et al., 2003).

(a) (b) (c)

Figure 2.8: Types of steel balls as grinding media available in the market such as (a) steel balls, (b) chrome steel balls and forged balls

Metallurgical efficiency can be improved by finer grinding, but at the expanse of higher media consumption and grinding energy. If steel ball over size, crushing force becomes strong, this will lead to penetrability crushing and make ore over crush. The valuable minerals in the ore will be difficult collected if the ore crushed too fine (Xiao et al., 2014). If steel ball under size, hitting force becomes lighter, this will make ore less fine. The selection of proper media will be able to improve the efficiency of fine grinding. Hence the economic limit of grinding has to be evaluated wisely because of ore of low value and high milling cost (Wills, 2006).

2.3.2 Tungsten carbide ball

Tungsten carbide is an unbelievable material as shown in Figure 2.9. Tungsten carbide was developed for use to cutting tools, moulds, dies and other abrasion resistant products in machine tools applications (Tsai, 2011). It is extremely hard at 1500 VHN with 30kgf loading or in the range of 16-22 GPa and fracture toughness of 13 MPa·$m^{1/2}$ (Kwade and Schwedes, 2007; Arif et al., 2011). This material is very wear resistant, with some abrasion tests showing it at 30 times of hard steel. It has good long term dimensional stability which makes a good material for gage applications.

Figure 2.9: Tungsten carbide balls as grinding media (Ma, 2016)

Tungsten carbide is extremely stiff, with a Young's modulus of elasticity to the extent of 550-720GPa, compared with steel at 207 GPa (Dash and Nayak, 2015). This high stiffness makes tungsten carbide balls a good choice for grinding media. Tungsten carbide is very good performance at temperature up to 427°C make it good choice in high temperature applications. It has high density (15.6x10^3 kg m^{-3}), high thermal conductivity (29-121 W/m K) and high compressive strength (5 GPa at 20°C), also have high oxidation and corrosion resistance. Others properties such as density, hardness, Young's modulus and wear resistance are shown in Table 2.2 (page 27) .

Usually, tungsten carbide ball was fabricated with die pressing method. The Tungsten carbide powders were waxed in paraffin wax as binder, then cold compacted at 400 MPa, dewaxed at 400°C in high purity hydrogen gas for 40 min, and finally sintered from temperature of 1260 to 1340°C with soaking times from 5 to 20 min (Sun et al., 2003). Tungsten carbide is identified to be prepared via pyro metallurgical method involving reaction of tungsten metal with carbon at 1400-2000°C. The fluidized bed reduction process can also produced tungsten carbide which involves tungsten metal or WO_3 with CO/CO_2 mixtures and H_2 at temperature between 900-1200°C (Dash and Nayak, 2015). Other preparation methods are heating WO_3 with graphite immediately at 900°C or in hydrogen at 670°C. It was followed by carburization in argon at 1000°C and then chemical vapour deposition method (CVD) involving tungsten halides and carbonaceous in hydrogen medium at 350-670°C (Dash and Nayak, 2015).