A COMPARATIVE STUDY ON THE EFFECT OF CHEMICAL ADDITIVES ON CLINKER GRINDING

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by

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **'A Comparative Study on The Effect of Chemical Additives on Clinker Grinding'**. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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Witnessed by

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Date:

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LIST OF ABBREVIATIONS

Al_2O_3	Aluminium oxide
As_2O_3	Arsenic trioxide
BaO	Barium oxide
CaO	Calcium oxide
Cr_2O_3	Chromium (III) oxide
CuO	Copper (II) oxide
et al.	and others
etc.	and more
Fe_2O_3	Iron (III) oxide
GA	Grinding Additive
GC	Gas chromatography
GeO_2	Germanium dioxide
HgO	Mercury (II) oxide
In_2O_3	Indium oxide
i. e.	that is
ITZ	Interfacial Transition Zone
K_2O	Potassium oxide
Lu_2O_3	Lutetium oxide
MnO	Manganese (II) oxide
MoO_3	Molybdenum trioxide
MS	Mass spectrometry
PbO	Lead (II) oxide
PSD	Particle Size Distribution
Rb_2O	Rubidium oxide
SEM	Tabletop Scanning Electron Microscope
SiO_2	Silicon dioxide
SrO	Strontium oxide
SO_3	Sulfur trioxide
TEA	Triethanolamine
TiO_2	Titanium (IV) oxide
TIPA	Triisopropanolamine

V_2O_5	Vanadium pentoxide
XRD	X-Ray Diffraction
XRF	X-Ray Flourescent
Y_2O_3	Yttrium oxide
ZnO	Zinc oxide
ZrO_2	Zirconium oxide

LIST OF SYMBOLS

°C	degree celcius
%	percentage
µ	micron

KAJIAN PERBANDINGAN MENGENAI KESAN TAMBAHAN KIMIA TERHADAP PENGISAR KLINKER

ABSTRAK

Matlamat kerja penyelidikan ini adalah untuk meningkatkan prestasi klinker dengan menggunakan pengisar bebola skala makmal untuk menghasilkan pengikat mineral berkualiti tinggi dari segi saiz zarah, bentuk zarah dan penghabluran zarah. Eksperimen telah dijalankan dalam keadaan kering, dengan 1 kg sampel klinker simen disukat menggunakan silinder penyukat dikisar dengan 20 kg bebola keluli. Pencirian dilakukan kepada sampel suapan dengan Pendarfluor X-Ray (XRF), Pembelauan X-Ray (XRD) dan Mikroskop Elektron Pengimbasan (SEM). Proses pengisaran dijalankan tanpa dan dengan penambahan Triethanolamine (TEA) dan dua bahan tambahan pengisaran industri, MA. G. A/C379 dan MA. G. A/C188 telah digunakan dalam eksperimen ini dengan dos 0.05, 0.25, 0.50 dan 1.00 wt.%. Didapati bahawa penambahan alat pengisar dengan jumlah alat pengisar yang berbeza-beza tidak mempunyai pengaruh yang ketara ke atas penjanaan serbuk simen bersaiz halus, mengikut graf taburan saiz zarah. Tambahan pula, zarah-zarah yang terbentuk adalah bentuk butiran memanjang, padu, bersudut, rombus, mengelupas, dan tidak sekata dan telah ditunjukkan bahawa tiada perbezaan yang ketara kerana bentuk butiran yang dicapai sebelum dan selepas mengisar adalah hampir sama. Kehabluran zarah produk tanah juga tidak berubah dengan ketara. Sebagai rumusan, didapati bahan tambah pengisar optimum yang boleh digunakan ialah MA. G. A/C379 dan MA. G. A/C188.

A COMPARATIVE STUDY ON THE EFFECT OF CHEMICAL ADDITIVES ON CLINKER GRINDING

ABSTRACT

The aim of the present research work is to improve the clinker performance by using a laboratory-scale ball mill to generate a high-quality mineral binder in terms of particle size, particle shape, and crystallization of particle. The experiment has been carried out in dry conditions, with around 1 kg of cement clinker sample measured using a measuring cylinder was ground with 20 kg of the steel ball. Characterization was done to the feed samples by X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The grinding process were run without and with the addition of Triethanolamine (TEA) and two industrial grinding additives, MA. G. A/C379 and MA. G. A/C188 were employed in this experiment with dosages 0.05, 0.25, 0.50 and 1.00 wt.%. It was found that the addition of grinding aids with varied amounts of grinding aids has no significant influence on generating fine-size cement powder, according to the graph of particle size distribution. Furthermore, the particles formed are elongated, cubic, angular, rhombus, flaky, and irregular grains shape and it has been demonstrated that there is no significant difference because the grain shape achieved before and after grinding is nearly identical. The particle crystallinity of the ground product is also not noticeably changed. To summarise, it was found that the optimum grinding additives that can be used are MA. G. A/C379 and MA. G. A/C188.

CHAPTER 1

INTRODUCTION

1.1 Background of Cement Grinding Process

Cement manufacturing in the globe today accounts for around 1.6 billion tonnes per year, and the grinding process consumes over 2% of all electricity generated globally. Clinker grinding requires around one-third of the energy necessary to create one tonne of cement. For electricity generation, this amounts to a particular power consumption of 57 kWh/t and a specific carbon dioxide emissions intensity of 9.1 kg carbon dioxide per tonne. Furthermore, the grinding of raw materials, coal, and clinker consumes 60-70% of the total electrical energy needed in a cement plant. As a result, even little improvements in grinding efficiency may lead to a considerable saving in plant's operation costs as well as reductions in greenhouse gas emissions.

In dry ball milling of fine powders such as cement grinding, a typical phenomenon is the slowing down of breakage as the powder turns finer, as the grinding efficiency diminishes with the accumulation of fines in the mill content (Hashim & Hussin, 2018). Grinding Portland clinker causes the crystal structure to develop new microcracks. The ionic bonds in crystals break as a result of defects, and the grains gain a lot of surface energy. Because of this phenomenon, cement granules develop positive and negative charges on their surfaces, causing them to interact and create an undesirable agglomeration. Most cement samples under evaluation had a consistent composition of 95% Portland clinker and 5% anhydrite (by mass). Using this method, it is possible to evaluate the impact of each grinding aid on the properties of the produced binder.

The cement particles have the ability to seal the armour plating, agglomerate coat the grinding medium, and form tiny plates that absorb impact. The action of the grinding media within a rotating mill not only crushes the existing clinker particles, but also strongly compresses them, resulting in the development of electrostatic surface charges of opposite polarity. As a result of the forces of attraction acting on them, the cement particles then agglomerate. Consequently, agglomeration of the cement particle lowers the grinding efficiency. This phenomenon is defined by a rise in energy usage while maintaining constant Blaine. The characteristics of the materials to be ground, the mill's operating parameters, the efficiency and distribution of the grinding media, the fineness of the cement particles, and the mill's internal operating conditions (humidity, temperature, ventilation, condition of the armour plating, etc.) all affect how much agglomeration occurs.

Interest in high performance cements has increased recently as a natural result of the production of high-performance concrete. Cement manufacturers are being asked to provide hydraulic binders with high early strengths to the market, which may be achieved by optimising numerous factors including clinker chemistry and reactivity as well as cement particle size distribution. It might be challenging to produce such high-performance cements at an affordable cost (in terms of clinker content and energy needs for high fineness grinding), which makes the addition of suitable cement additives necessary. Several types of products may be available on the market. The best option is based on a thorough analysis that considers all of the cement's characteristics, regardless of the additive employed. Pure grinding aids, particularly created to increase production and fineness, or performance enhancers with an influence on cement hydration (Magistri et al., 2010).

In the cement grinding circuit, clinker makes up about 95% of the feed, and the remaining feed consists of "additives," which includes grinding additives (GA). The surface area of cement is used to measure its quality (Blaine index). It should be noticed that the size distribution of the cement particles influences the surface area of cement powder in view of the fact that smaller particles have larger surface area. Grinding aids are crucial since the agglomeration situation remains to be a concern for cement producers. This makes it possible to partially neutralise surface charges that have formed during milling (Katsioti et al., 2009).

1.2 Problem Statement

Despite the industry producing a large number of grinding additives, a thorough understanding of grinding aids in clinker grinding is still lacking. Even though the fundamental mechanisms by which grinding aids function have been well known, the implementation of these aids still highly depends on empirical findings. Particularly, finding a grinding aid that increases efficiency is still almost impossible since several factors interact to make it difficult to derive the right selection criteria.

However, one of the major disadvantages of dry grinding is the high energy consumption, which is around 20-25% greater than that of wet grinding (Bruckard et al., 2011; Feng and Aldrich, 2000; Kanda et al., 1988; Ogonowski et al., 2018). Additionally, dry grinding is characterized by low material transport in the pneumatic pumping system which result in a low throughputs (Feng and Aldrich, 2000; Kanda et al., 1988; Ogonowski et al., 2018). Bruckard et al. (2011) discovered that particle agglomeration rises during dry grinding, affecting the downstream separation process. From any operation point of view, dry grinding poses a considerable danger of noise and dust pollution (Kanda et al., 1988; Ogonowski et al., 2018).

1.3 Research Question

1. What are the properties of the grinding additives that make it suitable to be used as an additive in cement grinding process?
2. What are the differences and similarities between ground products with and without grinding aids?
3. What are the optimal conditions for the clinker grinding to produce a good quality cement?

1.4 Objectives of Research

Main objectives will be as follows:

1. To study the effect of different type of grinding additives and dosage to the efficiency of clinker grinding.
2. To find the optimum conditions for the clinker grinding in order to produce a good quality cement.

1.5 Scope of Study

This research is being carried out to improve the grinding efficiency, by using various grinding additives. The experiment begins with feed preparation, which includes several processes, and is followed by grinding and characterization tests. Throughout the experiment, certain ball mill operating parameters, such as speed, grinding time, media size, and material remained constant. Furthermore, the mass of the media ball, the mass of the sample and the filling ratio used in the experiment all remain unchanged.

Meanwhile, triethanolamine (TEA), MA. G. A/C188 and MA. G. A/C379 used as grinding additives in varying amounts ranging from 0.05 to 1.0 wt.%. To ensure that the liberation process occurs effectively, the sample has characterized to examine the particle's crystalline structure, particle size distribution, and particle shape before and after grinding. For characterization tests, X-Ray Fluorescence (XRF), sieve analysis test, X-Ray Diffraction (XRD) and Tabletop Scanning Electron Microscope (SEM) are conducted.

The goal of the research is to determine the significant operation of the ball mill, dosage, and types of grinding additives for cement clinker grinding in order to produce a high-quality cement for industrial use. This is to ensure that the cement manufacturer is capable of producing high-quality products following industry standards. As a result, a grinding process using a ball mill with optimal parameters has carried out.

1.6 Contributions and Industrial Relevance of the Current Research

The use of grinding aids is critical for the manufacturing of high-performance cements required for high-quality concrete. Grinding aids have a significant chemical effect on cement hydration, in addition to their positive effects on agglomeration reduction and mill efficiency. Several parameters must be considered in order to enhance cement performance. The chemical and mineralogical composition, clinker grindability, gypsum content, and cement fineness are perhaps the most important. If a grinding aid is employed during cement manufacture, the optimal gypsum might be substantially different. This provides for interesting results in terms of increased compressive strengths and improved performance (Magistri et al., 2010).

In order to improve grinding efficiency, additives like water, organic liquids, and some inorganic electrolytes have been used to lower the surface free energy of the material being ground. The primary purpose of grinding aids is to minimize cement particle agglomeration, although they can also help with the following: (1) Complete or partial removal of the "coating" effect on the medium. (2) A rise in the fluidity of tiny particles, which increases separator effectiveness. (3) A reduction in pack-set issues in bulk delivery trucks and storage silos. (4) An improvement in bulk and bag cement quality. (5) Better material handling (blowing into silos, unloading trucks, etc.) due to increased fluidity. (6) Increased capacity for grinding production (Katsioti et al., 2009).

1.7 Thesis Outline

I. Chapter 1: A brief overview of the research

- A general explanation of the research's background, as well as a brief description of the scope of study and the research's purpose.

II. Chapter 2: A review of the literature on research studies

- Analyze and explain in detail the comminution process, hydraulic binder, grinding technology, fine grinding breakage mechanism, ball mill parameters, grinding additive types, and characterization methods used in this research.

III. Chapter 3: Methodology of experimental work

- A detailed description of the experiment will be carried out based on the objectives selected, including an explanation of the sample and grinding additive preparation, equipment setup (ball mill), and characterization analysis methods to be used.

IV. Chapter 4: Analysis data and results in discussion

- Interpretation, explanation, and comparison of the experiment's data and results obtained from all the characterization tests that are performed.

V. Chapter 5: Conclusion and recommendation

- Summarize the research findings and make recommendations for improving the experiment so that the data and results obtained are more accurate and reasonable for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Hydraulic Binder

Binder are substances which are used to bind inorganic or organic particles and fibers together to form strong, rigid and flexible components. This is often caused by chemical reactions that occur when the binder is heated, combined with water or other substances, or simply exposed to air. The water-activated cements used to create current building concretes are commonly referred to as "hydraulic binders" because they can set and harden in liquid water without requiring to remove excess water and because they harden through a reaction that requires water. The term also indicates that they can be utilized for underwater concreting under certain conditions.

However, the definition of "hydraulic binder" might lead to rather arbitrary distinctions between binders that are suited for usage in different types of humid environments. For example, gypsum plasters can set and harden in a modest excess of water but exhibit poor long-term performance under humid environments, due to the high-water solubility of the hydrated cement matrix (gypsum). However, the hardening process in this situation includes an interaction with liquid water to generate stable solid hydrates, and the existence of some excess water at early ages has no impact on the process. This clearly indicates that capillary forces are not the main bonding mechanism, as is sometimes wrongly assumed. As a result, we shall use the term "hydraulic binders" to refer to all water-dispersed binders that can harden initially in the presence of a modest excess of liquid water, even though not all of them are acceptable for long-term usage under water or in high humidity conditions. Other processes, such as atmospheric carbonation in the case of limes or polymer interdiffusion (film formation) in the case of latexes, may also be at play in many nonhydraulic water-dispersed binders, but physical removal of water from the material is always a necessary part of the early hardening process for such binders (Gartner & Macphee, 2011).

The binding mechanisms and the particle behavior as well as the characteristics of the processes and the resulting agglomerates are the same whether they are occurring in the processes of modification of powders and production of composites (Pietsch, 2002). Because hydraulic binders are essential components of concrete, the most frequently used building material, they play an important role in economic and social development.

2.1.1 Portland Cement

Because of its properties and widespread availability, Portland cement is now the most often used hydraulic binder. Cement is an ultra-fine grey powder that combines sand and rocks into a concrete matrix. It is the bonds that hold much of our contemporary global infrastructure together. Concrete is the second most consumed substance on the earth, after only water, with over one tonne used per person each year. Cement is generally made of calcium carbonate from calcareous rocks such as limestone, silica, alumina, and iron oxide from argillaceous rocks such as clay or shale (Syed et al., 2008).

Cement manufacturing consumes a significant quantity of nonrenewable raw materials and energy, and it is a carbon-intensive process. The binding mechanisms and the particle behavior as well as the characteristics of the processes and the resulting agglomerates and leads to ball coating as shown in Figure 2.1.

Figure 2.1 Ball coating without grinding additives

The cement is made up of dispersed solid particles with sizes ranging from 0.1 to 250 m. Particle size, particle size distribution, and cement composition all have an impact on its behavior during wetting, on the development of microstructures and on the properties of concrete or cement-based materials. Portland cement particle sizes must fall within particular limitations in order to be properly moistened and create a material with appropriate subsequent behavior. More, Excessive grinding leads to additional energy consumption (sometimes unjustified), whereas insufficient grinding might influence the binder properties of the cement particles and their distribution in the final product (Cristian et al., 2020).

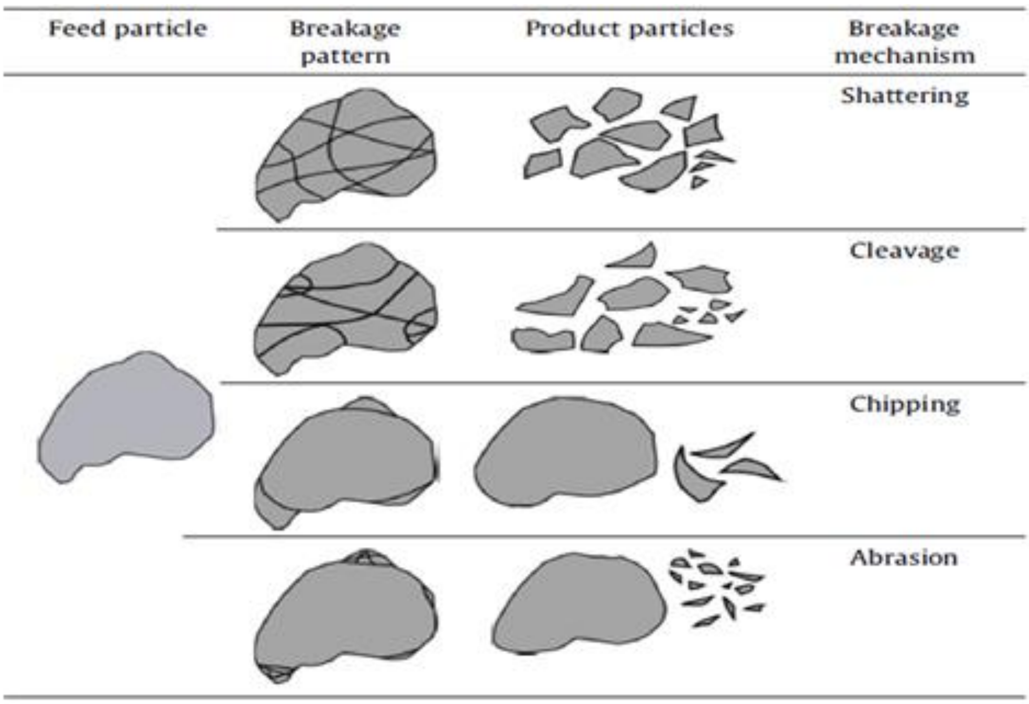
2.2 Grinding Technology

Grinding is a final stage of the comminution process, and it produces fine products with particle sizes of up to 300 µm. At this stage, particles are reduced in size using a combination of abrasion and collision. A grinding mill is a machine that breaks down solid materials into smaller pieces (Napier-Munn & Wills, 2005). Grinding is a precise material removal technique employed to enhance the size, and surface texture of a wide range of products. Grinding has grown in recent years as a result of its ability to achieve high removal rates and exceptionally high accuracy, frequently beating all other manufacturing processes. Grinding is a strategic process since it is the final machining operation that regulates the quality and surface integrity of finished goods. It is the most important stage of manufacturing since it is essential for achieving high productivity, precision, and quality.

Grinding is the most important step in extracting valuable minerals from gangue, and it has improved over the last 50 years by using tumbling mills. Conventional mills have been used for many years because they are relatively simple devices and continuous, high-throughput machines that are easy to control in order to produce the desired product particle size distribution. Grinding mills are widely used and have grown in popularity over the years, with the largest ball mills presently in use measuring 6.5 metres in diameter (Wills, 1990). Grinding process is required when size reduction of below 5-20 mm is needed. Grinding is the powdering or pulverizing process of various minerals (Barite, Calcite, Limestone, Quartz, Gypsum, etc). The primary goal of grinding is to increase the surface area of the material and generate a material with the necessary grain sizes and pulp resources (Balasubramanian, 2017).

Grinding media is a term used to describe the size-reducing materials used in grinders, such as metallic balls, rods, and so on. When the material passes through this media, it undergoes a huge size transformation in a large rotating uniaxial tumbler under the intense effect of gravity (Kapadia, 2019). Table 2.1 shows some of the mechanisms that occur inside operational grinding mills, such as abrasion, cleavage, shattering, and chipping. Additionally, when an operational variable is changed, these mechanisms become more visible. These acts will have an impact on particle formation. Grinding technologies such as the ball mill, planetary mill, and ring mill will also be used. Each grinding machine performs a specific operation, resulting in different particle sizes (Lomovskiy et al., 2020). The conventional comminution equipment has a limitation on achieving the fine particle size and requires a lot of energy. The comminution circuits alone consume 50–60% of the energy in a typical mineral processing plant (Deniz, 2011).

Table 2.1 Breakage mechanisms in a comminution process (Semsari Parapari et al., 2020).



2.3 Ball Mill

The ball mill is a common type of fine grinder. It is composed of a slightly inclined or horizontal rotating cylinder that is partially filled with balls, generally stone or metal, which grind material to the required fineness by friction and collision with the tumbling balls. Ball mills typically run with a ball charge of around 30%. Ball mills are characterized by their smaller (comparatively) diameter and longer length, which is frequently have a length 1.5 to 2.5 times the diameter (A. Balasubramanian, 2017). Ball mills are mostly used for fine grinding in a single stage, regrinding, and as the second stage in two stage grinding circuits. Ball mills can be either wet or dry designs depending on the needs of the customer. Ball mills are designed to produce finished products with standard size varying from 0.074 mm to 0.4 mm. The machine is partially filled with the material to be ground and the grinding medium usually stainless-steel balls as shown in Figure 2.2. They are suited for grinding hard materials, the end product shape is circular, there is no pollution for the powder with ceramic ball, stable performance, and capacity and fineness can be varied by modifying the diameter of the ball (A. Balasubramanian, 2017).

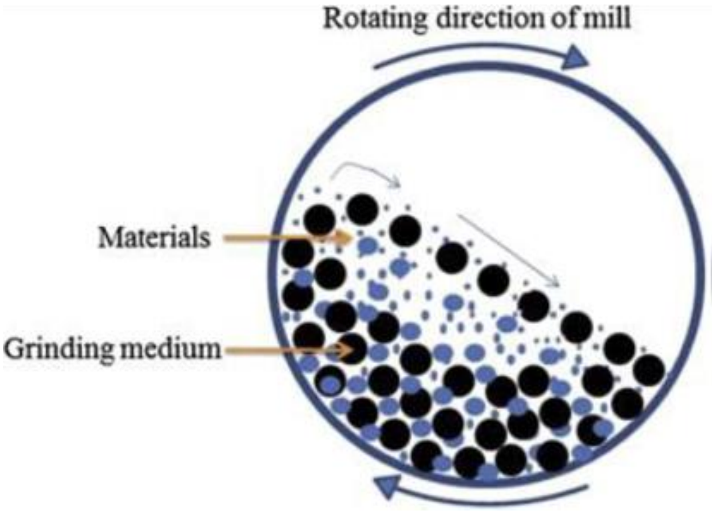


Figure 2.2 Schematic diagram of ball mill.

2.4 Grinding Environment

In mineral beneficiation, wet grinding is considerably preferable compared to dry grinding, but the rising shortage of water poses a danger to mining activities, especially in arid locations. Sweden has set aims on enhancing resource efficiency and reduction of water consumption in mining activities through dry beneficiation and exploring for alternative methods (SIP STRIM, 2019). Among other disadvantages, excessive energy consumption remains a key issue for dry grinding, as seen in Figure 2.3. This involves the development of energy-saving technology and strategies.

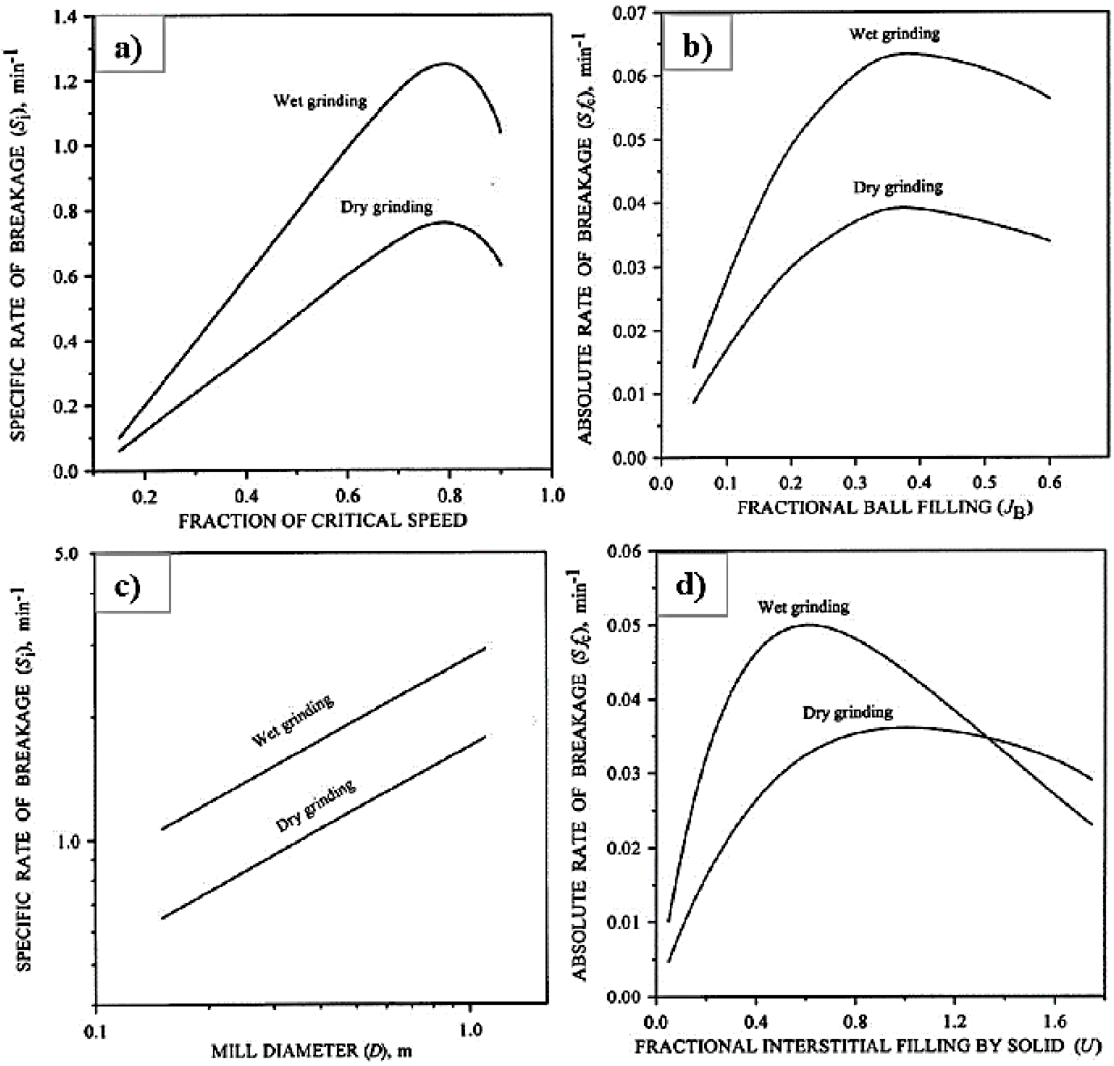


Figure 2.3 Comparison of dry and wet grinding breakage rates with varying a) mill critical speed, b) mill ball load, c) mill diameter, and d) mill interstitial filling after (Ozkan et al., 2009).

Grinding efficiency is affected by rheological properties, which mostly depends on the grinding environment. Grinding in wet condition, especially with water, is believed to be more efficient compared to grinding in a dry condition (Fuerstenau, 1995). Several researchers attribute this to water's physicochemical interaction with a ruptured surface bond, which facilitates crack formation (Lin et al., 1968). Although the economics of the application are unfeasible, grinding in organic liquids has been proven to be more effective than water (Fuerstenau, 1995). Grinding aids are influenced by the degree of mixing, temperature, slurry pH and solids percentage (Klimpel, 1978).

2.4.1 Dry systems

The particle-particle interaction increases as grinding duration rises resulting in agglomeration, which in turn lowers material flowability (Prziwara et al., 2018). Poor material flowability leads material buildup in the mill, allowing for the agglomeration of ground particles (Noaparast & Rafiei, 2003). During dry grinding, these conditions are further intensified. The surface charges on the particles are neutralised by grinding additives, which lowers inter-particle contact and fluidizes the substance (Altun et al., 2015).

2.4.2 Wet systems

There is a critical viscosity or slurry yield value in wet grinding systems when excessive fines and high solids content cause the grinding efficiency to drop significantly (Ma S et al., 2010). Above this critical viscosity, the grinding medium begins centrifuging (sticking to the mill walls), which has an impact on the cataracting and cascading motion in the case of tumbling mills. As a result, grinding additives function by lowering the slurry yield point and removing the centrifugal force. The deviation from Newtonian slurries (where shear stress is directly proportional to rate of shear) that results from a decrease in material flow characteristics typically leads to an increase in viscosity (Fuerstenau et al., 1995). The efficiency of grinding has been observed to decrease as viscosity increases. Grinding additives increase material transport by reducing pulp viscosity (Noaparast & Rafiei, 2003).

2.5 Process Parameters

A proper analysis of the impacts of process parameters on GA performance was given by Prziwara et al. (2018). They highlighted the significance of both material properties and mill "machine related factors". There is no published research on the effectiveness of using grinding aids in relation to direct machine parameters or grinding force (loading mechanism). However, few studies have focused on stress conditions, which are factors related to machines.

2.5.1 Grinding media type and size

Some research looked at the impact of grinding additives on grinding media with an emphasis on the type of material and size (Weibel & Mishra, 2014).

Grinding with cement additives decreases the coating of the grinding media, lowering the cushioning effect of particles and boosting the impact of the grinding. The impact of grinding additives on different grinding media consisting of alumina, steel, and zirconia was examined using grinding balls of various diameters with densities of 3.62,7.86, and 6.07 kg/l, respectively (Prziwara et al., 2018). Regarding the GA selection, grindability was shown to be unaffected by material ang grinding media size. Based on the product fineness and specific energy, it was determined that the alumina grinding media was the best choice because it resulted in less stress-energy and less energy (heat) dissipation because of its low density. The influence of material flowability (due to the application of grinding additives) is said to become crucial for mass capturing once the critical size (a size that permits the least amount of mass capturing based on particle size) is exceeded. Due to features such surface roughness, which may affect flowability, grinding media material is expected to have an influence on grinding. However, there haven't been any reported investigations (Farber et al., 2009).

The selection of material for grinding media is also essential to guarantee that the grinding additives do not erode the media (Lartiges & Somasundaran et al., 1992). The use of oleic acid as a grinding additive for fine quartz grinding with metallic balls did not result in an increase in grinding efficiency. This was attributable to the oleic acid-metal reaction, which consumed the grinding additives due side reactions, decreasing the amount of oleic acid available for grinding (Yusupov et al., 2010). Routray and Swain discovered that the GAs-grinding media interaction achieve a beneficial influence on the wear of steel balls. This observation can be attributable to the slurry's enhanced fluidity, which minimizes frictional wear on the grinding media (Routray & Swain, 2019).

2.5.2 Mill feed and solids content

When grinding a taconite ore with sodium hydroxide, Hartley et al. (1978) discovered that a feed with a narrow (uniform) size increased grinding efficiency compared to a feed with a wide range size.

Hartley et al. (1978) found that a feed with a narrow (uniform) size increased grinding efficiency compared to a feed with a wide range size in the grinding of a taconite ore with sodium hydroxide. According to their findings, the use of grinding additives is more effective on narrow PSD feeds compared to the widespread PSD feeds. It has been claimed that grinding additives are more effective at a high slurry concentration or solids content (Prziwara et al., 2018). Grinding efficiency for calcite with polyacrylic acid was 31.61 and 37.27 % for 60 and 70 wt. % solid percentage, respectively. This implies that grinding aids work better at greater solid concentrations (Choi et al., 2010).

2.5.3 Shear rate

Slurry shear rates for two types of ball motion inside a grinding mill, cascading and cataracting, have been estimated. Morrell's power model technique was used for the first kind of motion.

In this representation the charge made up of ‘shells’, with a mean width characteristic of the size distribution of the charge. The relative velocity between two adjacent shells of a 4.57 m diameter ball mill was determined to be 0.058 m/s. To determine the distance over which this change in velocity occurs, the present author's holdup model (Shi,1994) was used and simplified to compute the total slurry volume retained in the active charge. The number of balls in the active charge determined the contact area between the slurry and the balls in the active charge. The average distance between adjacent shells might be estimated using the total slurry volume and the active charge's contact area. For the above ball mill, the shear rate caused by the cascading motion was thus predicted to be 13 s^{-1}.

Therefore, it was predicted that the shear rates inside a ball mill would range between 13 and 730 s^{-1}. In order to characterize the apparent viscosities of slurries in grinding applications, shear rates in this range should be used. The methods given in this study can be used to calculate values for particular mills and operating conditions (Shi & Napier-Munn, 1997).

2.5.4 Dosage strategy

Several research have been conducted to compare the effect of the grinding additives dosage strategy in grinding, comparing continuous and once-off addition (Enustun et al., 1987). Stage-wise addition has reportedly been found to be more successful than single-stage addition, although this is not conclusive (Prziwara et al., 2018). At the onset of grinding the material is coarse (low specific surface area) with too much grinding additives (high flowability) which is undesirable but rather continuous addition the total quantity of grinding additives increases with an increasing fineness (specific surface area) which provides optimum flowability (Hartley et al., 2009).

2.6 Grinding efficiency evaluation

Few research has been conducted to investigate the influence of grinding aids on grinding performance. Grinding efficiency is often described in terms of mill throughput and specific energy consumption depending on the end product. Kokolev (1968) studied the effect of organosilicon (0.005 wt. percent) in the context of wet grinding of alumina in a ball mill, discovered that the grinding time was reduced four-fold when compared to grinding without any grinding aid.

Because of the significance of particle-particle interactions during grinding, more energy is required for further size reduction, reducing grinding efficiency. Grinding efficiency is primarily measured by the amount of energy required per unit mass of material as a function of time. It has been proven that grinding additives minimizes energy consumption. The reduction in energy consumption is increased by raising the dosage of grinding additives to a maximum, beyond which further addition has no effect.

In the cement industry, fineness is generally described by surface area rather than size dispersion. In fact, clinker grinding processes are frequently monitored and controlled off-line by measuring the product surface area using a simple air-permeability procedure like as the Blaine test. As a result, modelling the relationship between surface area and size distribution would be desirable (Zhang & Napier-Munn, 1995).

2.7 Mechanism of grinding additives

Grinding involves numerous and simultaneous sub-processes that can be classified as transporting material to the grinding zone, loading or stressing material leading to fracture, preventing material agglomeration, and transporting material away from the grinding zone. Some of these processes have been reported to be affected by the use of grinding additives in grinding. The grinding process, as shown in Figure 2.4, may be simply stated as a process that involves the transportation and capture of particles in the grinding zone as well as the application of mechanical stress to yield breakage.

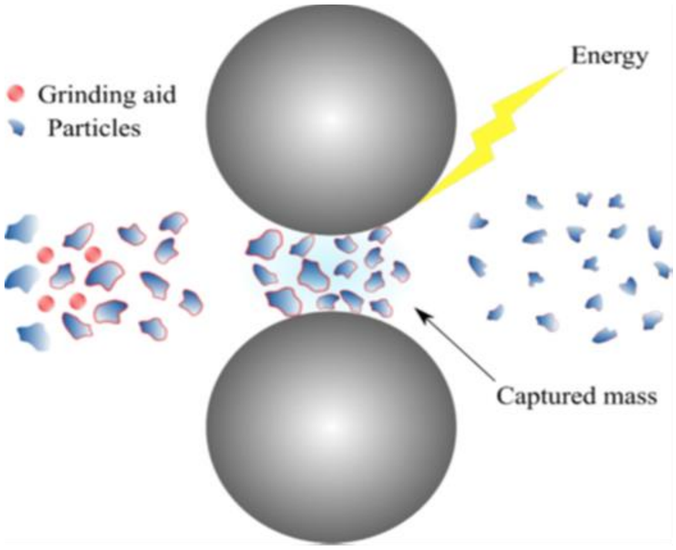


Figure 2.4 A schematic illustration of the particle capturing between grinding media in relation to the material flowability (V Chipakwe et al., 2020).

The mechanisms of grinding additives during grinding can be roughly classified into two kinds. The first is changes in the surface and mechanical properties of individual particles, such as surface energy (i.e. the Rehbinder effect) and surface hardness. Other than that, changes in particle arrangement and material flow characteristics through flocculation/dispersion, or prevention of agglomeration or control of material flowability.

Despite the difficulty of determining the adsorption mechanism empirically, it has been reported that adsorption of the grinding aid onto the particle surface is requisite for all of the proposed mechanisms. This adsorption has been agreed to occur through the following ways where hydrogen bonding, especially for particles with near-neutral surface charges, chelating bonding with metal ions, hydrophobic bonding through the hydrocarbon tail, and electrostatic bonding.

2.8 Influence of grinding additives on product properties

As surface active GAs are mostly adsorbed on the product particle surface even after grinding, it is not surprising that the additives have further effects on the final product properties or processing properties of the ground material. When cement particles are ground into smaller particles, they acquire positive and negative charges. These charges cause the cement particles to agglomerate as shown on Figure 2.5, making them easier to adhere to the ball mill surface (Fayza et al., 2019).

There have been a few theories put forth regarding how GAs work, and they are primarily based on two principles: (i) the chemical and physical impact on specific particles, such as surface energy reduction (Rehbinder and Kalinkovaskaya,1932), and (ii) the impact on particle arrangement and material flow properties (Klimpel and Manfroy, 1978; Locher and Seebach, 1972). The influence of GAs on rheology is often recognised as the primary mechanism. However, no empirical evidence supports this statement. All of these conditions have highlighted how crucial flow characterization studies are when grinding additives are taken into account. The use of grinding aids has revealed that there is an optimal dose for specific conditions, which are dependent on both material properties and process conditions. This shows the procedure's intricacy, which may be attributable to the dynamic nature of the grinding process (Prziwara et al., 2018).

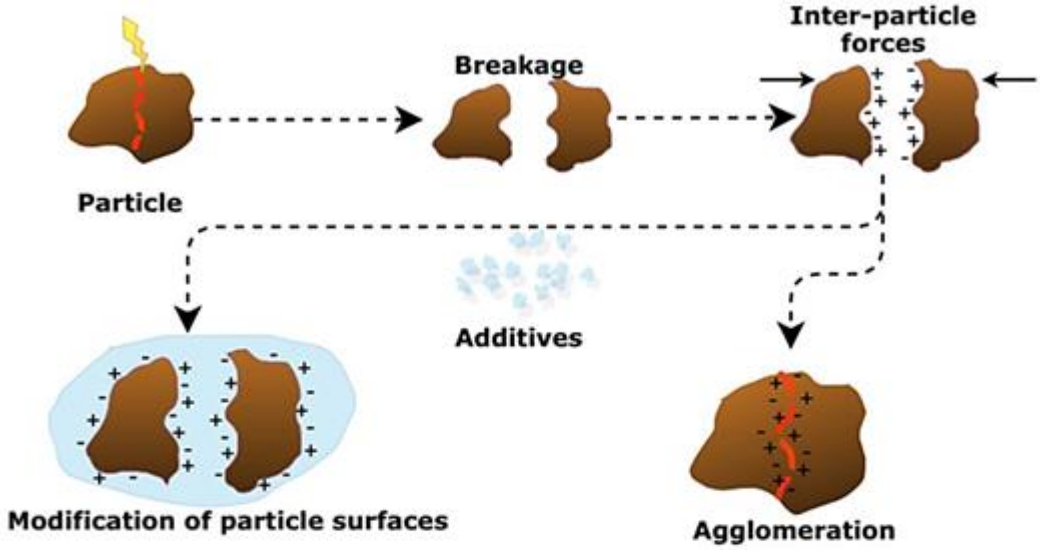


Figure 2.5 Effect of grinding additives on particle surfaces

Furthermore, these impacts are particularly well-known in the field of construction materials. Thus, the most essential of these factors are highlighted, because they may limit the selection of appropriate grinding additives while also resulting in significant improvements in terms of product quality.

2.8.1 Construction materials

Especially in the field of construction materials, the effects of residual grinding additive molecules on the handling capabilities of the ground materials during the further processing as well as on the final product properties are important. The reason for this is that they may reject even additives that result in excellent grinding results. As a result, a number of research have previously been conducted to study the influence of GAs on these aspects. The most major impacts may be roughly classified into three aspects which are in terms of processing properties, chemical hydration reaction and the hardening of the paste, as well as the development of strength and the final strength of the construction component.

Numerous studies have shown that grinding additive molecules maintain their stabilizing properties even when ground particles and water are mixed. This has a considerable impact on the particle paste's rheological characteristics, such as viscosity and spreading behavior, as well as the water requirement (Assaad & Issa, 2015). However, the impact of chemical additives on the chemical hydration process when combining a fine particle binder (such as cement clinker) with water and other filling materials, as well as fine and coarse aggregates, is of main interest in the field of cement chemistry.

The kinetics of these reactions define the paste's setting behavior and consequently its processability, particularly in terms of time for mixing, transferring, putting, and compacting. Several research have already explored and discussed the influence of residual GA molecules on the hydration process and subsequent setting behavior (Kong et al., 2012). Furthermore, GAs may affect the strength of the final building component by modifying the hydration process and reaction products. In fact, the bulk of the research articles that investigated GA influences on the dry grinding of cementitious materials studied the additives' influence on strength development simultaneously (Sandberg & Doncaster, 2004).

2.8.2 Other examples

Aside from the construction sector, further consequences of GA molecules on product qualities are only sporadically reported. For instance, Toraman et al. (2016) shown that specific grinding additives had an impact on the colour attributes of ground calcite, such as the lightness, total colour difference, and whiteness index. These impacts are also unrelated to the final product fineness. Furthermore, according to Badjena(2011), GAs have an impact on product attributes like gloss and surface characteristics when applied to brass particles and pigments. Last but not least, GAs can have a considerable impact on the bulk density of fine powders (Prziwara et al., 2020), which may be critical for later supply chain activities such as packaging and shipping. Although this problem has not yet been investigated in scientific research, it is well known from industrial grinding applications that it should be taken into account when choosing a GA since, in the worst scenario, prevent certain compounds from being utilized as GA.

2.9 Grinding additives

Grinding aids are surface active chemicals that help in particle comminution during the milling process. Grinding aids are added in modest amounts, ranging from 0.01 to 0.10 percent by weight of cement in the production of Portland cement, according to the PN-EN 197-1 standard (Bensted et al., 2009). They allow the material to obtain a larger specific surface area in a shorter grinding time, reducing energy consumption. According to the literature, even a small amount of these agents can increase mill efficiency to 25%.

Chemical grinding additives are organic chemicals that are added to the grinding process in order to. Grinding additives, also referred to as grinding aids, are organic substances that are added to the mill during the grinding of cement to increase the rate of size reduction and, at the same time, increase the grinding efficiency and lower the amount of energy needed to grind the clinker to a given fineness (Magistri et al., 2010). These terms are frequently used in the cement industry, in order to enhance the throughput to the mill. The first commercial grinding additives were used in the cement industry in the late 1930s, which marks the beginning of the history of grinding aids in dry fine grinding processes. Since then, grinding additives' significance in industrial dry fine processes has greatly expanded.