# A study on the relationship between cement particle size distribution and strength development

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Thesis to obtain the Degree in

## Mining and Geological Engineering

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## Declaração

Declaro que o presente documento é um trabalho original da minha autoria e que cumpre todos os requisitos do Código de Conduta e Boas Práticas da Universidade de Lisboa.

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## Abstract

The objective of this work resides in the study of the relationship between the particle size distribution of the cement that makes up the mortar and its influence on the development of its compressive strength. Since the beginning of the use of cement, new and different fields of application have been implemented in the world, thus increasing the demand for cements with different specifications and properties. But producing cement is an extremely expensive and environmentally damaging activity. This study is dedicated to finding an energy efficient (and therefore also economically) way to produce a cement that is competent with the established requirements, focusing on the problem of milling, the costliest and least efficient process in cement manufacturing.

Thirteen preliminary tests were carried out to determine the most efficient way to reach the target PSD, in which different combinations and variations of the key parameters for the energy efficiency of the milling were tested: milling time, milling body load, pre-milling of the material and non-stick additive (grinding aid functioning as an anti-binder agent). After comparing the percentage of fines (final residue and passing percentage) present in the samples tested, a milling system was established with the most efficient conditions.

With the samples obtained in the grinding, eleven mortar specimens were manufactured and were subsequently cured in a humid chamber. The flexural and compression tests carried out on the specimens showed that their compressive strength is higher as the curing time increases and their proportion of particles between 63 and 125μm is greater.

**Key words**: cement milling, ball mill, energy efficiency, PSD, compressive strength.

## Resumo

O objetivo deste trabalho reside no estudo da relação entre a distribuição granulométrica do cimento que compõe a argamassa e a sua influência no desenvolvimento da resistência à compressão.

Desde o início da utilização do cimento, novos e diferentes campos de aplicação foram implementados no mundo, aumentando assim a procura de cimentos com diferentes especificações e propriedades. Mas produzir cimento é uma atividade extremamente cara e prejudicial ao meio ambiente. Este estudo dedica-se a desenvolver uma metodologia eficiente em termos de energia e que permita redução da energia elétrica e consequentemente do seu custo na fatura energética, produzindo um cimento que não perca as características de resistência. Esta tese foca-se no problema da moagem em moinhos de bolas, o processo mais caro e menos eficiente na produção de cimento.

Uma série de testes preliminares foram realizados para determinar a forma mais eficiente de atingir a distribuição granulométrica objetivo, nos quais diferentes combinações e variações dos parâmetros-chave para a eficiência energética da moagem foram testadas: tempo de moagem, padrão de carga de moagem, pré-moagem do material e aditivo tensioativo. Após comparação da percentagem de finos (resíduo final e percentagem de passagem) presentes nas amostras de cimento fabricadas, foi estabelecida uma metodologia de moagem com as condições mais eficientes.

Com as amostras obtidas na moagem, foram confeccionados provetes de argamassa que posteriormente foram curados numa câmara húmida. Os ensaios de flexão e compressão realizados nos provetes mostraram que sua resistência à compressão é maior à medida que o tempo de cura aumenta e que a proporção de partículas entre 63 e 125μm é também superior.

**Palavras-chave**: moagem de cimento, moinho de bolas, eficiência energética, PSD, resistência à compressão.

## Scope

The degree of fineness of the material used (cement) influences the characteristics of the mortar or concrete, among them and being the most notable for its importance, the compressive strength.

This study is dedicated to the investigation of the compressive strength of mortar related to its PSD. For this, the process involves the manufacture of cement with material (clinker and gypsum) coming directly from the factory, its milling and classification by size, that is, according to its PSD. This study works to determine suitable milling conditions to generate an appropriate PSD of cement for the manufacture of the target specimens, at the same time that this process is energy efficient (taking into account the problem of energy inefficiency in the cement sector, in concrete in the milling process).

The specimens made with selected cement are subjected to compression tests, in which, together with the granulometric analysis previously carried out on the cement samples, it is intended to understand the possible relationship between PSD and its compressive strength.

Used machinery, although treated as equivalent to represent the industrial setting in the most similar way, does not meet certain characteristics of industrial machinery. Therefore, laboratory limitations in the milling process are not solved in this research.

This study is a first approach to the relationship between PSD and compressive strength. From the data and conclusions of this study, it would be advisable to draw new experiments for the verification and concretization of the interpretation of the results.

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## List of acronyms and symbols

| | | | |
|---|---|---|---|
| **BC** | Before Christ | **EN** | European standard |
| **C** | Clinker | **HPGR** | High pressure grinding rolls |
| **CIMPOR** | Cimentos de Portugal | **VRM** | Vertical roller mill |
| **CO2** | Carbon dioxide | **UNE** | Spanish standard |
| **PSD** | Particle size distribution | **NP** | Natural pozzolan |
| **ISO** | International organization for standardization | **NP** | Norma Portuguesa/Portuguese Standard |
| **FMC** | Fineness modulus of cement | **GGBFS** | Ground granulated blast-furnace slag |
| **G** | Gypsum | | |
| | | | |

## 1. Introduction

Production of cement is an energy-intensive industry in which the milling circuits consume around 60% of the total electrical energy of the manufacturing process (Figure 1), representing a very high and specific energy consumption of this stage (Genç, 2016). In general terms, cement production consumes 2% of global primary energy and 5% of total global industrial energy. In addition, this high energy consumption means that it is in this phase where most of the cement manufacturing cost is located (Osorio et al., 2013).

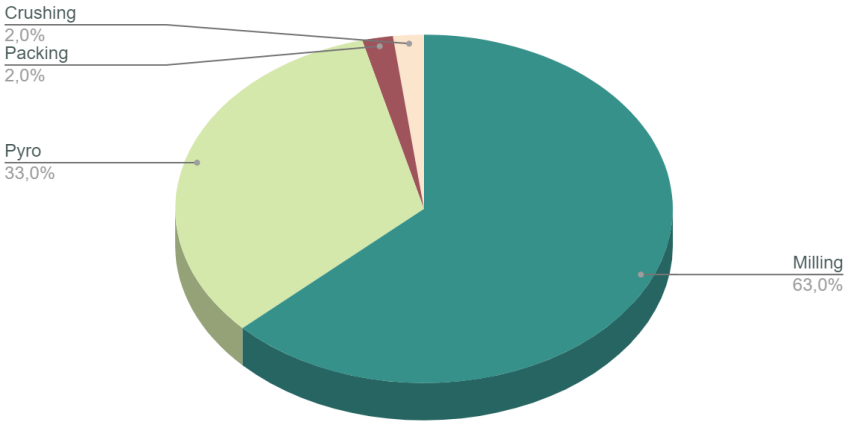


Figure 1: Power consumption in the diverse areas of a cement plant (adapted from Jankovic et al., 2016).

Due to the consummate importance of international environmental awareness as well as the high costs involved in supplying energy to industry, operational and functional systems have been investigated and created to ensure that industries carry out their activities in the most sustainable way possible, thus saving in electricity consumption and therefore also cutting on costs. The cement sector tries to carry out its activity by developing profitable projects both economically and environmentally, and for this reason it is currently taking measures such as increasing the use of renewable energies (e.g. use of biofuels) and investing in research. Still, more precise changes are needed to achieve a sustainable cement manufacturing process (IGME, 2009). The main requirements of the sector for a more efficient and sustainable future are the reduction of energy use in grinding and also the emission of $CO_2$ from the kilns. Substantial economic and environmental benefits can be achieved by operating under optimal process conditions, equipment design, or implementation of new process alternatives (Genç, 2016).
Within these fields of studies, the variables that can affect the productivity and energy efficiency of the process are many, among them are the air flow rate through the mill, the operation of the classifiers, the rotation speed of the mill, the ball charge size and loading, additives (grinding aids) and correctors or the feed flow rate (Osorio et al., 2013).

## 1.1 Outline

Clinker is obtained from the calcination at 1.450°C of a mixture of primarily limestone, clay and iron ore. The product of the calcination process is clinker - the main ingredient in cement - which is finely ground with gypsum and other chemical additives to produce cement (CEMEX, 2020).

From IECA (2017), the Spanish Institute of Cement and its Applications, it is known that the average composition of a portland cement (the different types of cements will be discussed in section 2.2) would be: 64% calcium oxide, 21% silicon oxide, 5.5% aluminium oxide, 4.5% iron oxides, 2.4% magnesium oxide, 1.6% sulphates, 1% other materials, among which mainly water.

Cement has unique physical properties depending on the proportion of main raw materials that make it up, on the amount of secondary raw materials that have been added to the mix, and also on the additives that have been incorporated. There are, from the point of view of standard composition, two types of components:

- A main component of cement is determined as an inorganic material, specially selected and mostly used, which indicates the designation of the type of cement.
- A minority component is any main component, used in a proportion of less than 5% by mass with respect to the sum of all the main and minor components (IECA, 2017).

In fact, the main function of the addition of other minority components or additives to the paste in the global cement industry is small variations in the physical properties of cement, such as compressive strength or workability. There are additives internationally established by the standard UNE EN 934-2 for different purposes:

- Water reducers (fluidizers).
- Superfluidizers (superplasticizers).
- Setting accelerators.
- Set retarders.
- Hardening accelerators.
- Water repellents.

The particle size distribution (PSD), which specifies the proportion of fine and coarse particles in the cement, controls the hydration reactions, setting time and water demand, of the mortar created from the cement, as well as how it influences the physical and mechanical properties that the mortar will have. “A narrower cement PSD results in a lower packed density and a higher voidage. A slender PSD is characteristic of cement produced in more efficient grinding systems such as vertical roller mills and modern closed-circuit mill systems equipped with third-generation separators” (IECA, 2017). Different types of cements are necessary for different types of functions, and that is why a variation is made in their composition, PSD or production process to achieve a cement that conforms to the required requirements as closely as possible (Ghalandari & Iranmanesh, 2020).

Three fundamental factors described so far must be taken into account:

- The high energy consumption produced by the operations necessary to produce cement.
- The problems derived from this consumption in terms of high economic costs and environmental impact.
- The relationship between the PSD of the cement and its resistance to compression, the main characteristic that measures the quality of a cement.

It is therefore interesting to carry out an investigation that relates these factors, being able to evolve to a more sustainable and economical cement production, through the properties that its composition confers on it, specifically in particle size and its proportions.

## 1.2 Objectives

The main objective of the study was to test the existence of a correlation between the development of the compressive strength and the percentage of fine particles (equal to or less than 45μm) in a mortar specimen. To achieve this objective, thirteen preliminary tests were carried out to determine the most efficient way to reach the target PSD, in which different combinations and variations of the key parameters for the energy efficiency of the milling were tested: milling time, milling body load, pre-milling of the material and non-stick additive. After comparing the percentage of fines (final residue and passing percentage) present in the samples tested, a milling system was established with the most efficient conditions.

This study evaluated how the granulometric curve of the cement affects the compressive strength of the mortar, with the intention of obtaining resources to reduce the electrical consumption of cement grinding without losing the properties necessary to obtain a quality mortar that is competent with the evolutionary needs of society.

The experimental method as well as the materials and facilities used in the experiment are reported in the chapter 4 “Materials and methods”, providing detailed information on the processes and the steps followed.

The results obtained after experimentation are exposed in chapter 5 “Results” and are discussed in relation to other investigations and advances registered to date in chapter 6 “Discussion”.
This discussion will be expository, so that first the results, values, variations, alterations... observed in the calculations will be discussed and then these data will be compared with scientific articles and relevant information related to the subject, in order to draw conclusions advantageous over the experiment and determine a future area of study.

The following diagram shows in a summarized and visual way the development and points of connection of this thesis.

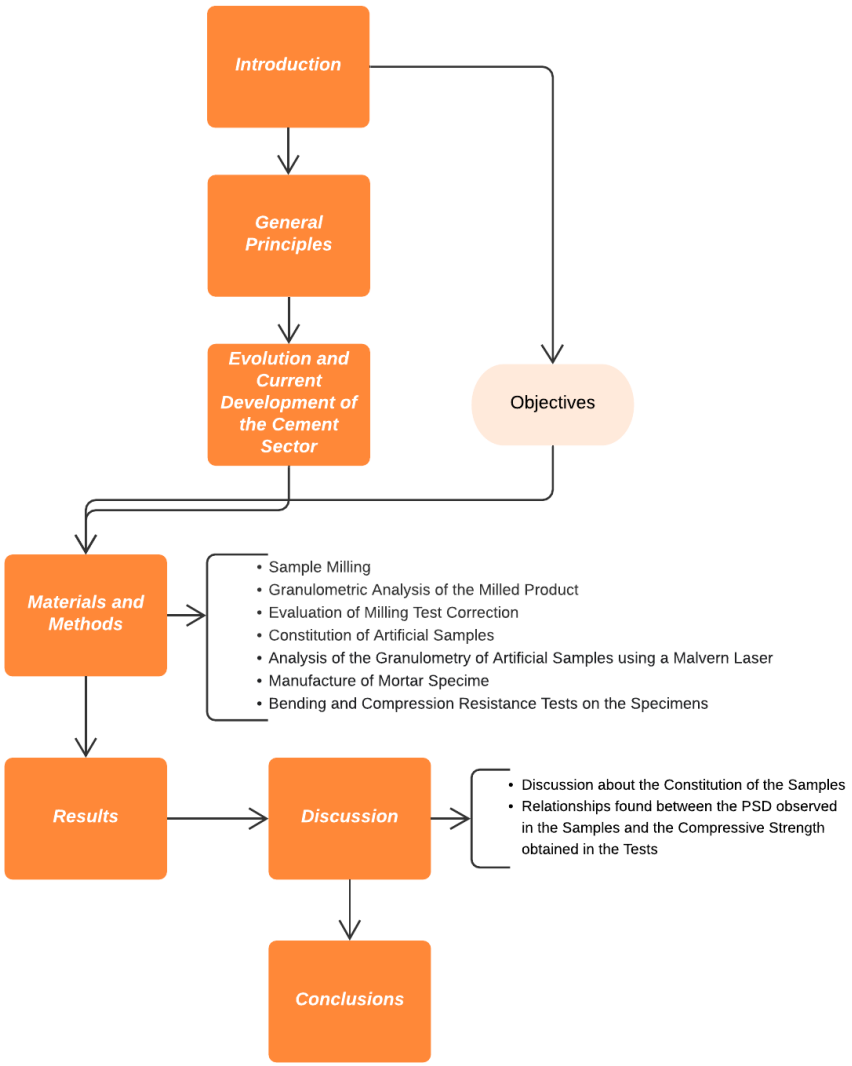


Figure 2: Scheme of the common thread of this study.

## 2. General principles of cement production

In this section it is possible to see how the evolution of cement has been from its first preparation until today, the types of cement that currently exist and what are their differences, as well as the cement manufacturing process through its different stages and the machines used in said process.

### 2.1 The origin and evolution of cement

Cement is a finely ground inorganic, non-metallic powder, and when mixed with water it forms a paste that sets and hardens. Cement is a basic material for building and construction of civil works.

The use of cement and concrete (mixture of cement, aggregates, sand and water) in Europe has been done for thousands of years (Schorcht et al., 2013). Around 450 BC, Greek and Roman builders discovered that certain materials from volcanic deposits, mixed with limestone, sand and water, produce a mortar of great strength, capable of resisting the action of fresh and salt water. Some years later, around 100 BC, the Roman civilization used concrete in the construction of large buildings, and also in the drinking water network and in the evacuation of sewage. Buildings and architectural works of antiquity as relevant as the Pompeii amphitheatre, the Roman Colosseum, the Pantheon in Rome or the Salisbury Cathedral more recently, show in their structure the first uses of cement as a construction material (Oficemen, 2017).

Since the middle of the s. XVIII until the beginning of the s. XIX James Parker and Joseph Aspdin worked on the development of a new type of mortar to join blocks, finally patenting a new artificial hydraulic cement in 1824 (Schorcht et al., 2013), manufactured by the joint combustion of limestone and coal, which they named Portland Cement for its dark color, similar to the Isle of Portland stone. Due to the complex manufacturing process of this material, and the high costs derived from it, it was not widely used in the beginning. A few years later towards the end of the century, the industrialization process and the introduction of rotary kilns led to the extension of its use for all kinds of applications.

At present, notable technical improvements have been introduced in the characterization of Portland cement, thus improving its performance, despite this, this cement continues to be very similar to the first one that was patented. Today, concrete made with Portland cement admits multiple application possibilities, adjusting in a more specific and functional way the needs of society. All types of concrete have demonstrated over time their excellent properties and their high degree of durability and resistance, which can be seen in large buildings, public works or artistic ensembles, showing the functionality and good behavior of this aggregate of materials (Oficemen, 2017).

### 2.2 Cement classification: Portland cement and other types

Twenty-seven different types of cement are identified by the European standard EN 197-1:2011, which has been published in the Official Journal of the European Union on 19th June, 2012, C 176/1 (EUR-lex, 2012), approximately ten years after the first specification standard for a construction product within the scope of the Construction Products Directive, UNE-EN 197-1:2000, showed up

(Sanjuán & Argiz, 2012). All the types of cement are associated in five major groups (Table 1). In addition to these types, there is a special section for the range of cements produced for particular applications that are shown in the annexed section (Schorcht et al., 2013).

Table 1: The percentages of each type of cement supplied to national markets in 2005 in the EU-27 (adapted from Schorcht et al., 2013).

| Type of Cement | Unit | 2005 |
|---|---|---|
| CEM II Portland-composite | % | 58,6 |
| CEM I Portland | % | 27,4 |
| CEM III Blast furnace/slag | % | 6,4 |
| CEM IV Pozzolanic | % | 6 |
| CEM V Composite cement and other cements | % | 1,6 |

## 2.3 Cement production

The cement manufacturing process comprises four main stages:

1. Raw material extraction and preparation
2. Grinding of raw material
3. Kiln firing
4. Clinker milling and cement production

In this trial we focus particularly on the stage of milling the clinker (Figure 3) for the subsequent production of cement. It is at this stage where all the experiments carried out take place and which we will refer to later.

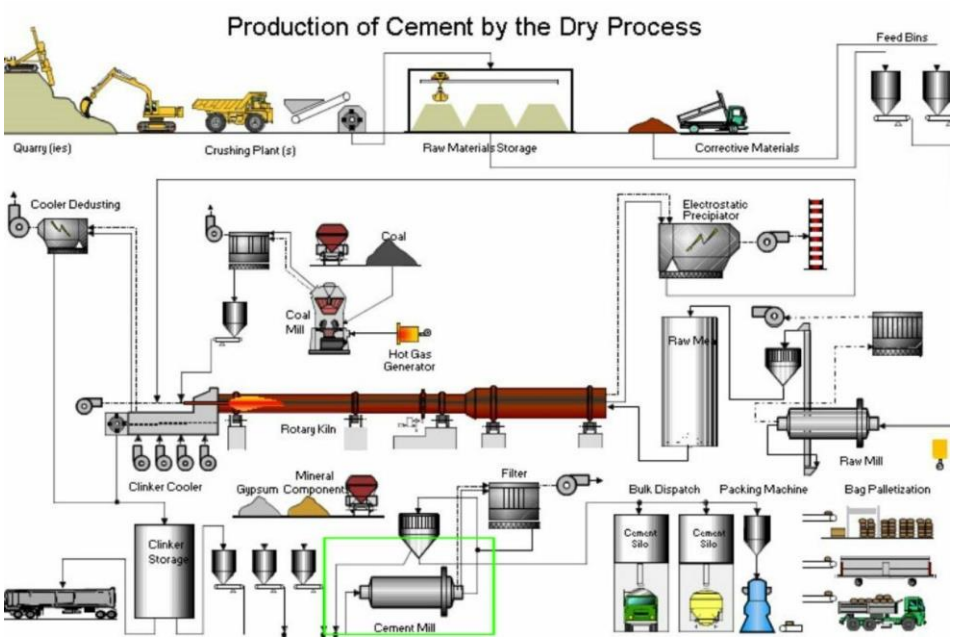


Figure 3: Graphical representation of cement production process (Altun, Benzer & Enderle, 2013). The part of the process corresponding to the present study, the milling of cement, is marked with a green rectangle.

### 2.3.1 Raw material extraction and preparation

The first phase that must be carried out in the manufacture of cement is the mixture of a good number of raw materials, the majority being limestone, followed by marl and clays (Figure 4), which mainly differ in the percentage of calcium carbonate in their composition (being limestone the one with the higher percentage, marl in the middle, and clay with the less percentage), and to a lesser extent by siliceous sands, pozzolans, bauxite, pyrite ash or other iron ores (IGME, 2009).

Figure 4: Pictures of limestone, marl and clay from left to right (IGME, 2009)

In the case of hard materials such as limestone and slate, the quarries are exploited through controlled blasting, while in the case of soft materials such as clays and marl, excavators are used for their extraction. All materials are transported to the plant by dump trucks and must be classified (Oficemen, 2017; CEMEX, 2020).

### 2.3.2 Grinding of raw material

With the raw material already extracted and classified, it is crushed and ground until obtaining a suitable granulometry for the grinding product. By means of conveyor belts or trucks, the material is transferred to the pre-homogenization park for storage. In pre-homogenization, the already crushed material is stored in uniformly arranged layers that allow controlled selection to prepare the appropriate dosage of the different components, reducing their variability.

After this storage period, the material is crushed to reduce its particle size and thus favour its calcination in the kiln. The material is re-stored in silos to increase the uniformity of the mixture (Oficemen, 2017).

### 2.3.3 Kiln firing

The properly prepared raw material is introduced to the kiln where it is transformed into clinker, in a process that consists of several stages. As the temperature in the system increases, the material is dried and preheated. Upon reaching temperatures close to 900 ºC, the crude mixture calcines, with the release of CO2 and the formation of CaO, from the CaCO3 found in the limestone, marl and clay. Subsequently, at temperatures between 1400 and 1500 ºC, sintering or clinkerization occurs, which involves the formation reaction of clinker minerals, from calcium oxide and silicon, aluminium and iron oxides.

These new minerals, also called clinker phases, are responsible for the hydraulic properties of cement. (Alite: C3S tricalcium silicate, Belite: C2S dicalcium silicate, Aluminate: C3A tricalcium aluminate and Ferrite: C4AF calcium ferroaluminate)
The clinker obtained is cooled with air at temperatures between 100 and 200 ºC, transported and stored in suitable tanks (IECA, 2017).

At the exit of the kiln, it is necessary to reduce the temperature of the clinker, for which it is introduced into the cooler, which by injecting cold air from outside makes the clinker decrease from 1,400ºC to 100ºC. The hot air generated in this device is introduced back into the furnace, so that the thermal energy created is not wasted and thus the energy efficiency of the process is improved (Oficemen, 2017).

### 2.3.4 Clinker milling and cement production

The clinker is mixed with gypsum (which acts as a set retarder) and other additives such as slag and/or ash inside a cement mill. In recent years, other alternative substances (chemical substances) have been increasingly used as additives, generally from other industrial activities that generate them as waste (IGME, 2009).

The mills can be roller and ball mills. The latter is the most used in world industry and consists of a large tube that rotates on itself and contains steel balls inside. The balls collide in between them and act as grinding bodies thanks to the rotation of the mill, crushing the clinker and additives until obtaining a fine and homogeneous powder: cement (Oficemen, 2017).

Various difficulties are frequently encountered in the milling of clinker and gypsum. The adhesion of the finer particles produced to the surfaces of the ball mill is one of the main problems encountered in the collection of said particles. For this, in the cement industry additives or grinding aids are used, whose function (due to their tested chemical composition) is to avoid this agglomeration of particles on the surfaces and allow a more efficient collection of the ground cement.

## 3. State of the art

As has been seen in subchapter 2.1 of this work; "The origin and evolution of cement" there are many contributions of new and modern scientific research that have led to the development of cement as we know it today. There are different categories of cements with properties and characteristics that improve the functionality of a specific system, as seen in subchapter 2.2 “Cement classification: Portland cement and other types”.

All these changes and advances in the sector have brought countless improvements to society in multiple areas, but the evolution and development of cement continues to expand.

In this section, the various and most recent advances that have been generated in the different areas of the cement sector will be commented and discussed, with the two main pillars of this work being the focus of attention: the energy efficiency of the grinding process and the impact of PSD in the compressive strength of the mortar.

### 3.1. Milling equipment

A brief description of the machines used in cement production and its characteristics and possibilities are described below.

#### 3.1.1 Ball mill

The main and traditional process equipment in grinding circuits for the manufacture of cement in the last 100 years have been multi-compartment ball mills and air separators for particle classification. Multi-compartment ball mills can be classified as (Genç, 2016):

• Single-compartment ball mills.
• Two- or three-compartment ball mills.

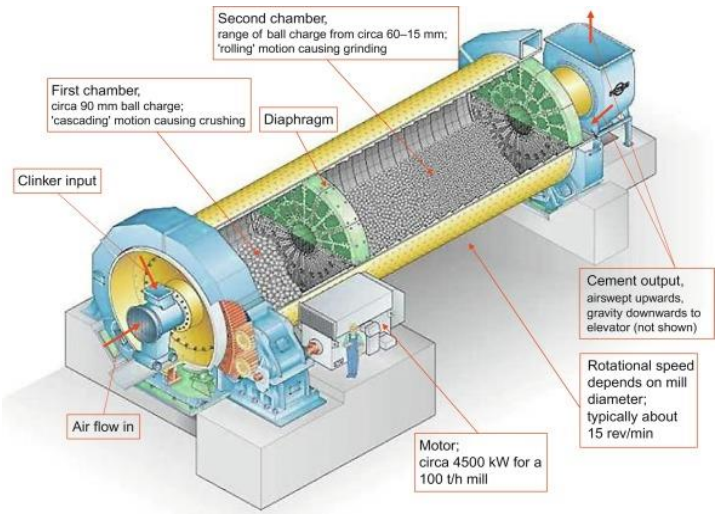


Figure 5: Diagram of a cement ball mill (del Strother, 2019).

The cylindrical shell of a ball mill is typically 1-1.5 times the diameter of the shell in length (Figure 4). As for the type of feed, it can be in two ways (although normally only the first is used):

I. Dry, with less than 3% moisture to minimize ball coating,
II. Wet (grout,) which can contain 20-40% water by weight.

The grinding bodies, steel balls with a diameter of 30 to 80 mm, occupy up to 40% of the capacity of the ball mill, which efficiently grind the ore. The material to be ground fills the gaps between the balls. Spinning balls capture the particles in ball / ball or ball / liner events and charge them to the point of fracture (Jankovic, 2015).
They are used in the crushing of cement raw materials (i.e. limestone, clay, iron ore), cement clinker, and cement additive materials (i.e. limestone, slag, pozzolana) and coal. Multi-compartment ball mills are relatively inefficient in size reduction and have a high specific energy consumption (kWh/t). Typical energy consumption is 30 kWh/t in cement grinding (Genç, 2016).

### 3.1.2 High pressure grinding rolls

High Pressure Grinding Rollers (HPGR) are used to reduce the size of rocks and minerals. They are most often used to process hard material, although they can also refine softer materials such as industrial minerals. Thanks to the two rotating rollers (one in a fixed position and the other one rotating) that are shown in Figure 6, they manage to compress the feed material between them.

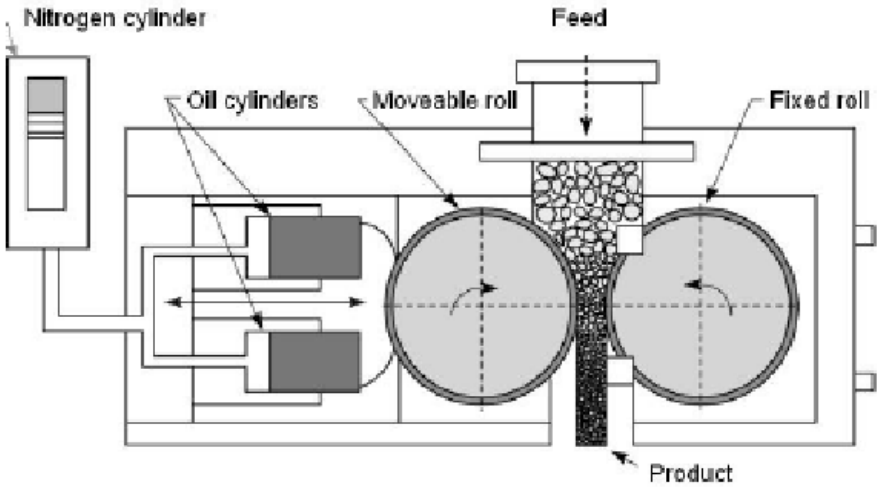


Figure 6: Schematic of HPGR (Jankovic et al., 2016).

HPGRs are known for efficient energy reduction, have a lower specific power consumption than ball mills, and require less space per unit and capacity at lower investment costs. They operate with throughput capacities of more than 300 t/h of crude cement mix.

This equipment reduces downtime through the use of robust components and long-lasting wear elements. In addition, its design allows a simple maintenance of the machine since it is possible to change critical parts easily (Genç, 2016; del Strother, 2019).

### 3.1.3 Vertical roller mill

For the past three decades the vertical roller mill (VRM) has emerged to be a suitable choice for grinding raw materials since it offers definite advantages over the ball mill system. In comparison with the ball mill, the VRM receives bigger feed size (40 to 100mm and can reach 120mm) and it can grind the material of particle size of 5% of the grinding roller diameter. In addition, the material is typically retained within the chamber for just one minute.

Another advantage is the decrease in noise pollution. The VRM emits 20 to 25dB. This equipment also requires less installation space, it has lower specific power consumption per ton of cement (40 to 50% energy savings in comparison with a ball mill) and it implies 30% less capital investment than ball mills. These mentioned peculiarities of the VRM are very positive, but without a doubt the best feature is its multifunctional character, i.e. simultaneous drying, grinding, homogenizing, separation and transportation. One single machine embodies all needed functions (Genç, 2016).

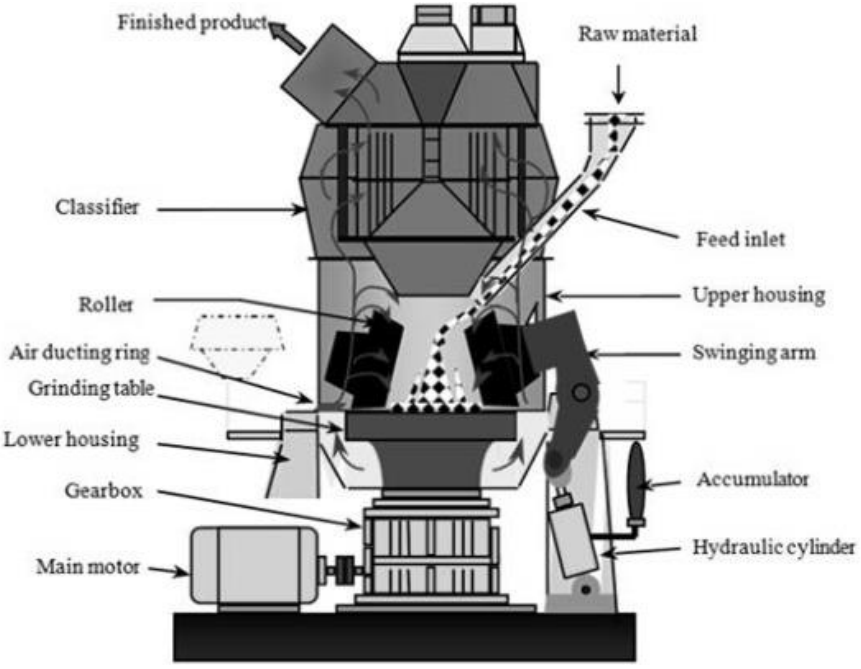


Figure 7: Schematic of VRM (Jankovic et al., 2016).

### 3.1.4 Stirred media mill

The fine and ultrafine grinding suffered an improvement in energy efficiency thanks to the technology and innovation brought by the agitated media mills, always having as a basis for comparison the traditional milling with ball mills.

Agitated media mills use smaller media than usual and operate at high fill rates. These media are stirred at high peak speeds. Thanks to these operating characteristics, energy savings are achieved in the process.

There are vertical and horizontal agitated media mills. The difference between the two lies in their operating characteristics, these being notably more favorable for the energy efficiency of the process in the case of horizontal mills.

"Horizontal agitation mills can operate with higher media filling (up to 85%), with higher agitation speed (6–22 m/s) and with a lower media size (1 mm)" (Altun, Benzer & Enderle, 2013).

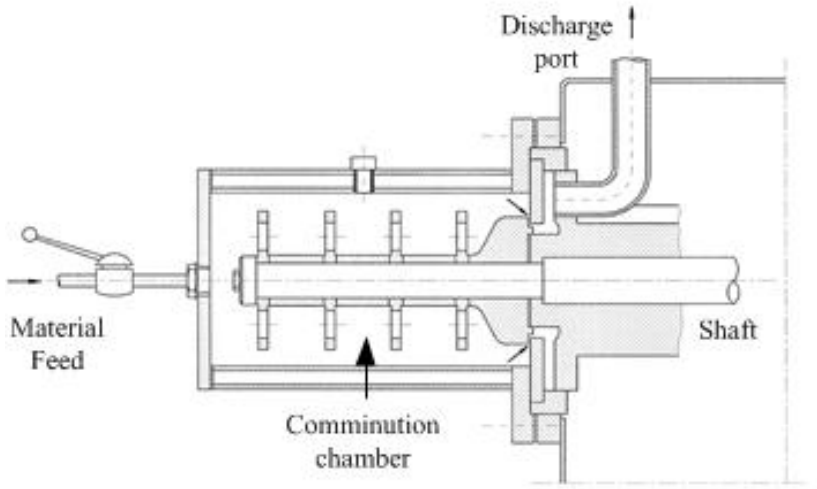


Figure 8: Horizontal stirred mill (Alvarado 2014).

## 3.2 Milling method

So far the cement production method has been reviewed in a very general way. The clinker milling process has been described and the different machines used have been seen with the differences between them. It has been observed that machines such as the Vertical Roller Miller or the High Pressure Grinding Rolls are more energy efficient options (in addition to other advantages such as initial cost and required space) than the traditional Ball Mill. Despite this, it is widely used around the world.

But does the entire weight of energy responsibility fall on the energy consuming machine or can this also vary depending on the milling method used in the process?

According to a 2006 study realized in Turkey by Binici et al., the milling method does influence both the energy efficiency of the grinding and the PSD obtained.

Two different types of milling are contrasted for a clinker base composition, ground granulated blast-furnace slag (GGBFS) and natural pozzolan (NP). This base composition is ground following two

mechanisms: separate milling and intermilling. The analysis of the results lead to the following conclusions:

I. The samples obtained from separate grinding were relatively finer than those obtained from intermilling.
II. In addition, the tests made on the specimens made with samples from both grinds revealed that the separate milling specimens lead to a higher compressive strength.

This study investigates the possible relationship between the PSD in a sample, specifically the content of fines smaller than 45µm, and the compressive strength.

In the 2019 del Strother article, they experiment with pre-grinding the compounds that make up clinker. It is claimed that the finer the grind, the more the electrical consumption of the mill increases, and therefore also increases the specific energy consumption of the furnace in the subsequent stage. "The specific fuel consumption of the furnace also increases because the smaller the particle size, the lower the efficiency of the cyclone from the preheater and the greater the recirculation of the powder from the furnace to the preheater." It should be noted that the mills used in this experiment are equipped with spacers to minimize over-grinding.
The negative effects of grinding quartz sand are also discussed, being this in the form of dust a significant danger to the health of workers. The improvement in the PSD of the ground material supposes in this case an additional expense in safety equipment in handling, storage and transport.

Another important parameter to take into account is the grindability of the clinker. Already in 1961 J. Osorio described in his article "Current concepts on cement grinding" this parameter as "the greater or lesser resistance that a clinker opposes to be ground", making it clear that grindability could be measured and the existence of devices on the ground for that purpose.

## 3.3 Preface of the compressive strength of a mortar

The compressive strength is usually the main property that is related with the cement quality, and it is also a fact to determine if a cement is one type or another.

There are different factors that affect the increase or decrease of the compressive strength in a mortar made with cement:

- Water-cement ratio: By reducing the a/c ratio of the hydrated cement paste, the cement particles get closer to each other, producing less capillary porosity and fewer free spaces for the development of hydration compounds that crystallize in the spaces of water off the cement particles.
- Coarse aggregate: The compressive strength of the aggregates cannot be less than the design strength of the concrete that it is intended to constitute.
- Fine aggregate: The mixture of natural sands from different sources allows optimizing its granulometry and achieving increases in resistance. In manufactured sands produced by

crushing, the shape of its particles and the increase in surface area can appreciably affect the demand for water, with the corresponding loss of strength.

- Cements: To the extent that you want to increase the resistance of concrete, the selection of cements to be used resistance is much more rigorous. Different Portland cements, which comply with all the standards and are essentially similar, may behave differently, when the water-cement ratios of the concrete in which they are used are lower than usual (Sepúlveda, 2011).

In this study the last section of the list is considered, the cement itself, measuring how different PSD cement samples would behave as to compressive strength.

### 3.3.1 Relationship between PSD and compressive strength

The compressive strength of the mortar is closely linked to the fineness of the cement and its mineral composition. It is known that as the fineness of a cement increases, the speed with which it hydrates also increases (Mehta & Monteiro, 1993). The range of sizes contained in the cement (used to make concrete) is also related, so that a cement with a narrower PSD has greater compressive strength than a wider PSD. Due to this, different studies have been carried out in relation to cement grinding, especially in the case of mixed cements. This section discusses the most relevant articles to date within these terms.

In the article by León and Hernández (2011) there is a comparative test of the compressive strength achieved by two mortar specimens with different compositions, at 7 and 28 days. The specimens were made following the NC 192: 2007 standard (Tables 2 and 3) and the compression tests were carried out following the NC 244: 2005 standard.

Tables 2 and 3: Concrete batching for the samples (León & Hernández, 2011).

| **M1** | | |
|---|---|---|
| **Materials** | **Theoretical Weight (kg)** | **Real Weight (kg)** |
| Natural sand from Arimao | 6020 | 5905 |
| Gravel Antonio Maceo | 6720 | 6759 |
| Cement Mariel P-350 | 2646 | 2650 |
| Chemical additive Dynamon SRC 20 | 21 | 22 |
| Zeolite | 294 | 290 |
| Water | 1085 | 1092 |

| M2 | | |
|---|---|---|
| **Materials** | **Theoretical Weight (kg)** | **Real Weight (kg)** |
| Natural sand from Arimao | 4690 | 4417 |
| Gravel Antonio Maceo | 5684 | 5747 |
| Cement Mariel P-350 | 2940 | 2921 |
| Chemical additive Dynamon SRC 20 | 14 | 12 |
| Zeolite | 0 | 0 |
| Water | 1190 | 1185 |

From the results observed in the experimentation (Table 4 and Figure 9) it is extracted that at 7 days a higher result of compressive strength was achieved in M2, which was influenced by the greater quantity of cement, which allowed the increase in resistance with respect to M1. However, at 28 days, no significant results were seen between the two samples, although in M1 the small increase was given by the role played by the zeolite in the mixture despite a lower cement content.

Table 4: Average values of compressive strength (León & Hernández, 2011).

| **Sample** | **Compressive Strength (MPa)** | |
|---|---|---|
| | **7** | **28** |
| **M1** | 23,7 | 35,6 |
| **M2** | 26,1 | 34 |

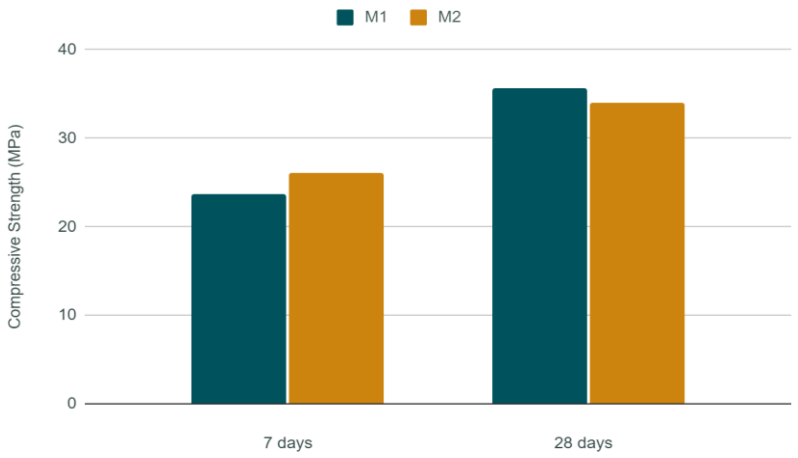


Figure 9: Average values of the compressive strength of the two samples expressed graphically (León & Hernández, 2011).

The compressive strength acquired by a mortar cured in a humid chamber, and therefore hydrated, increases as the curing time also increases. There are two factors that increase or favour compressive strength:

- Curing time in a humid chamber.
- Cement PSD; the greater the amount of fines present, the greater the compressive strength.

It is generally accepted that particles larger than 75μm are practically impossible to fully hydrate, while for particles larger than 45μm, hydration is possible, although it is a difficult process. To know exactly the relative reactivity rate of a cement, it is necessary to carry out an exhaustive study of its PSD. In the cement industry, PSD is measured by surface area, so that the relationship is that for an equal surface area, cements that have a narrower PSD range have a higher compressive strength (Oner, Erdogku & Gunlu, 2003).

As mentioned in subchapter 2.1, the demand for cements with different characteristics has evolved at the same time as this same one. Han et al. (2007) comments that the industry sometimes requires concrete with high compressive strengths, 5MPa, in very short curing times, 14 hours, for different purposes.

## 4. Materials and methods

Laboratory experiments were carried out in order to obtain data on the optimal characteristics of the grinding process of a cement sample and the relationship of the results obtained on the compressive strength of said cement.

Different ball patterns were used in the grinding of clinker and gypsum, which are explained in section 4.2.2 “Ball Charge Pattern”. In addition, in some tests an additive (i.e. surfactant) was added: MAGA C077 (supplier -MAPEI). The dose used at an industrial level is between 300-500 g/t.

Two different tests were carried out to determine the granulometric curve of each initial sample: screening and diffraction laser test. The reason for the use of this second is the verification and contrast of the data obtained with the screening.

Artificial samples were made with the material obtained from the preliminary mills. These samples are made up of different percentages of the same particle size, the particle size range being 45 to 125µm. Between 92-95% of the composition of these artificial samples are particles smaller than or equal to 45µm, the target size for mills.

The grinding tests were carried out at the Geolab (Department of Civil, Architecture and Georecourses, IST). The tests with the Malvern laser on the artificial samples were carried out at the Laboratório de Combustão (Department of Mechanical Engineering, IST). The flexural and compression tests, as well as the manufacture of the specimens, were carried out at the Laboratório de Construção (Department of Civil, Architecture and Georecourses, IST).

The mortar specimens for the experimentation were made following the Portuguese Standard (NP hereinafter) EN 196-1 “Cement test methods; determination of mechanical resistance”.
The workability tests carried out to characterize the mortar specimens were made following the UNE-EN 1015-3.

### 4.1 Materials

In this subchapter the materials and machinery used to carry out this experimentation are mentioned.

- Jones dividers of different sizes (cm): 48x49.5, 33.5x57, 26,5x32.5, 11.5x14
- Plastic bags
- Pre-grinding crusher
- Brushes, pans and paddles
- Denver mill (Table 6 and Figure 10)
- Phototachometer
- Sieves of different sizes (µm): 65000, 46000, 32000, 22400, 16000, 11200, 8000, 5600, 4000, 2800, 2000, 1400, 1000, 710, 500, 355, 250, 180, 125, 90, 63, 45 and 32 (Figure 13)

- Vibration screening machine
- Ceramic balls (Figure 15)
- Scale
- Laboratory furnace
- Malvern laser
- Programmable automatic mixer AUTOMIX (Figure 19)
- Specimens compactor machine (Figure 20)
- Specimens molds (Figure 20)
- Workability testing table and mold
- Bending and compressive press (Figures 22 and 23)

## 4.1 Sample

A clinker sample of approximately 20kg and a gypsum sample of 4.5kg were used, both brought directly from the cement-producing factory CIMPOR.
A 93% clinker and 7% gypsum composition was used (434,0g of clinker and 32,67g of gypsum).
For the division of the initial clinker and gypsum samples, different Jones dividers were used, depending on the size required by the maximum diameter of the pieces of material. The reason for using this device was to preserve as much as possible the original characteristics of the sample.

The samples were subdivided into smaller fractions until reaching an amount close to that needed in the tests. In the case of clinker, bags of approximately 600g were used. For the gypsum the bags were approximately 35g.

After completing the divisions of the original material samples into smaller portions, some samples were set up for testing following the aforementioned composition. These final samples were packaged and stored until used at the mill.

It should be noted that due to the results obtained in the first preliminary tests, it was decided to pre-grind the materials, both clinker and gypsum.
A screening of the material was carried out, in which the fraction of material with a size greater than 16000μm was separated. This fraction was introduced into the crusher for grinding. Thus, for both clinker and gypsum, the maximum material size was between 11200μm and 16000μm.

The objective of this phase is to make a detailed description of the characteristics relative to the particle size distribution, PSD, of the sample to be tested later. For this, a granulometric analysis of the sample is carried out, with a series of sieves equal to that used in the granulometric analysis after grinding (Table 5). The reason that both series are equal is precisely to facilitate the comparison of sizes and quantities of material before and after grinding.

In the first tests a more limited series of sieves, of only 8 sieves, was used and it was found that this exercise was insufficient to obtain an accurate granulometric curve. So more screens were added to the set, ultimately having a total of 22 screens in the process.

Table 5: Set of sieves used in the primary particle size analysis and an example of the results obtained from sample #13.

| Sieve opening (µm) | Weight retained (g) | Percentage retained (%) | Accumulated retained percentage (%) | Passing percentage (%) |
|---|---|---|---|---|
| 1000 | 0,00 | 0,00 | 0,09 | 99,91 |
| 710 | 0,40 | 0,09 | 0,18 | 99,82 |
| 500 | 0,80 | 0,18 | 0,35 | 99,65 |
| 355 | 1,40 | 0,31 | 0,66 | 99,34 |
| 250 | 3,40 | 0,75 | 1,42 | 98,58 |
| 180 | 5,70 | 1,26 | 2,68 | 97,32 |
| 125 | 16,90 | 3,74 | 6,42 | 93,58 |
| 90 | 9,50 | 2,10 | 8,52 | 91,48 |
| 63 | 36,10 | 7,99 | 16,52 | 83,48 |
| 45 | 29,10 | 6,44 | 22,96 | 77,04 |
| 32 | 198,80 | 44,01 | 66,97 | 33,03 |
| Pan | 149,20 | 33,03 | 100,00 | 0,00 |
| Total | 451,70 | 100,00 | | |

## 4.2 Experimental method

Preliminary tests were carried out to determine the most efficient cement milling system. For this, the different parameters that affect the process were taken into account: ball charge pattern, previous grinding of the mill feed material, milling time, additives, mill rotation speed and mass of the samples. These last two parameters are considered invariant since they depend on the characterization of the mill.

To analyse the impact of the variations made by altering the conditioning parameters, samples were screened to obtain the granulometric curves of the samples and thus visualize the PSD.
In this section, the conditions that were studied to carry out the characterization of the preliminary tests as well as the screening followed to analyse the impact of these conditions are explained.

This section also describes how each of the preliminary experiments was carried out, in other words, the method of execution of the experiment.

The process could be described in 7 parts ordered sequentially:

- Sample milling
- Granulometric analysis of the grinded product
- Sample storage and results observation
  Constitution of artificial samples
- Analysis of the granulometry of artificial samples using a Malvern laser
- Manufacture of mortar specimens
- Bending and compression resistance tests on the specimens

The tasks carried out in each of the stages are briefly described below from subchapter 4.2.3 to 4.2.9.

### 4.2.1 Milling process

The conditions of the study, mass and volume of samples to be ground, mass of the ball charge, and the specifications of the mill used are present in Table 6.

Table 6: Denver mill and conditions of the study specifications chart.

| | |
|---|---|
| Mill diameter (cm) | 30,48 |
| Mill length (cm) | 12,7 |
| Rotation speed (rpm) | 70,9 |
| Body load mass (g) | 9060,51 |
| Internal mill lining | Smooth |
| Type of milling | Dry |
| Feed volume ($cm^3$) | 291,67 |
| Feed mass (g) | 466,67 |

The rotational speed of the mill was measured in the initial experiments using a phototachometer. As shown in Figure 10, a reflection mark was fixed on the surface of the mill and the light beam from the phototachometer was directed at this mark. The resulting value was appended to the data of the milling process specified in Table 6.

Figure 10: Denver mill with the attached reflection mark for the rotational speed measurement.

The milling time was set according to CIMPOR regular industrial conditions; the process normally takes around 120 minutes.

For mill and media cleaning, the ball charge was introduced into the mill along with standard sand to remove remains of other materials, impurities and signs of oxidation that the balls could have and thus prevent contamination of the samples to be milled.

Several problems were detected in the grinding process of the clinker-gypsum mixture:
Due to the variety of size in the pieces that constitute the clinker fraction of the sample, the grinding time underwent notable variations as the samples were tested. The main problem was that larger pieces of clinker could not be ground to powder. This problem may be due to the lack of impact path that the grinding balls had due to the small size of the Denver mill. The Denver mill is a mill for laboratory tests, and therefore does not have the large dimensions that industrial mills have. This problem was also reflected in the granulometric curves obtained in the post-grinding analysis of the sample.

The other problem that was detected in the grinding phase was the inevitable loss of material in the cleaning process of the mill chamber. Although this was emptied and cleaned with extreme caution, the finest particles simply remained suspended in the environment or stuck to the imperfections inside the mill and the milling balls.

### 4.2.2 Ball charge pattern

Following the specifications of the mill, the ball charge pattern 1 was recreated, with 9,061kg of total mass. The following patterns were created from this mass condition.

Two main parameters were taken into account when determining the optimal milling characteristics from the results obtained:

- Milling time
- Milling ball charge pattern

Regarding this last parameter, it should be specified that several milling ball charge patterns were determined during the different tests. The specifications for each pattern are found in Table 7.

Table 7: Specifications on number and weight of each of the milling body load patterns used in the Denver mill.

| Ball diameter (mm) | 1 | | 2 | | 3 | |
|---|---|---|---|---|---|---|
| | Number of balls | Weight (g) | Number of balls | Weight (g) | Number of balls | Weight (g) |
| 48 | 4 | 1674,5 | 7 | 2791,1 | 5 | 2121,8 |
| 40 | 14 | 3155,1 | 17 | 3854,3 | 15 | 3492,6 |
| 30 | 28 | 2747,6 | 16 | 1506 | 22 | 2226,4 |
| 25 | 4 | 224,6 | 7 | 398,5 | 6 | 332,2 |
| 23 | - | - | 9 | 401,7 | 15 | 666,1 |
| 19 | 19 | 867,9 | - | - | | |
| 13,5 | 37 | 392,6 | 11 | 108,1 | 28 | 223,9 |
| **Total** | 117 | 9060,5 | 67 | 9059,7 | 91 | 9063 |

### 4.2.3 Sample milling

Milling is the most important phase in all experimentation since it is the producing phase of the material that is used later. Since several ball charge patterns have been used in this test (Table 7), it was necessary to detail which one was going to be used in each test to introduce it into the mill. With the built-in ball load, the sample was introduced into the Denver mill. The mill was then carefully closed with the help of a wrench. A digital stopwatch was used to set the grinding time and the process was started.

Many are the variables that affect the milling process and therefore, the PSD of the product. In this experiment these variables were changed in order to find which combination of them was more favourable for the desired PSD. In Table 8 it is shown how the variables changed during the preliminary tests. It should be noted that from sample #13 the variables were always kept constant, adjusting to the criteria shown in this test.

Table 8: Variable disturbance during the preliminary tests.

| Test sample # | Composition | Pre-milling of G | Pre-milling of CK | Grinding aid (drops) | Milling body load | Milling time (mins) |
|---|---|---|---|---|---|---|
| 3 | 93% CK, 7% G | ✓ | | | 1 | 60 |
| 4 | 93% CK, 7% G | ✓ | | | 2 | 55 |
| 5 | 93% CK, 7% G | ✓ | | | 2 | 55 |
| 6 | 93% CK, 7% G | ✓ | | | 2 | 120 |
| 7 | 93% CK, 7% G | ✓ | | | 1 | 120 |
| 8 | 93% CK, 7% G | ✓ | | | 1 | 120 |
| 9 | 93% CK, 7% G | ✓ | ✓ | 1 | 1 | 120 |
| 10a | 93% CK, 7% G | ✓ | ✓ | 1 | 2 | 120 |
| 10b | 93% CK, 7% G | ✓ | ✓ | 1 | 2 | 150 |
| 11 | 93% CK, 7% G | ✓ | ✓ | 1 | 3 | 120 |
| 12a | 93% CK, 7% G | ✓ | ✓ | 2 | 1 | 120 |
| 12b | 93% CK, 7% G | ✓ | ✓ | 2 | 1 | 180 |
| 13 | 93% CK, 7% G | ✓ | ✓ | 2 | 1 | 120 |

At the end of the milling, the mill was emptied. A funnel-shaped structure was used to facilitate the deposition of material from the mill to the collecting container (Figure 11). This same device has a grid in the upper part to prevent the grinding balls from straining together with the material.

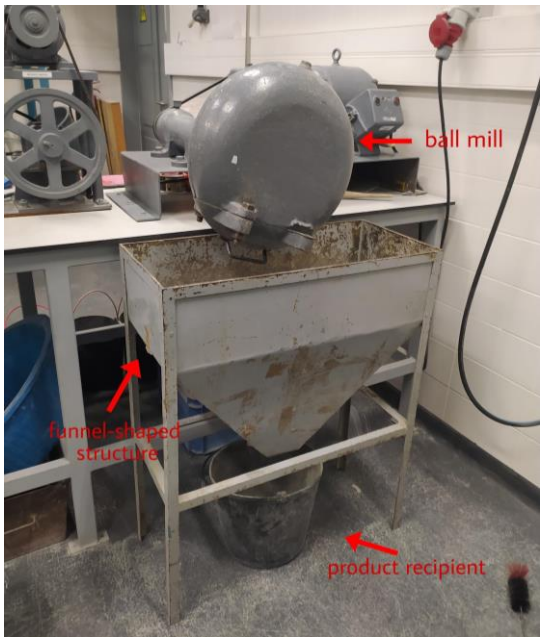


Figure 11: Disposition of ball mill and other apparatus when ready for emptying the mill.

The main problem in this stage was the aggregation of material on the porous surfaces both inside the mill and on the grinding balls. This problem was reasonably solved by cleaning the inside of the mill and all the grinding balls manually with the help of a brush. Even so, in this cleaning process, some of the finest particles were suspended in the air and were lost.

### 4.2.4 Granulometric analysis of the milled product

The analysis of the size of the particles generated as a product of the comminution is carried out to characterize the product. This measurement is called granulometric analysis.
The determination of the particle size generated by mineral comminution is commonly carried out by screening, either dry or wet, on a series of sieves with square openings, mounted on a vibrating apparatus.

The progression of openings between the various sieves obeys certain international standards regulated by the International Organization for Standardization, ISO, and specifically for metal mesh sieves are governed by the ISO 3310-1: 2016 standard.
Standard sieves are constructed with standardized wire diameters and thicknesses. The opening between a sieve and the one immediately following the series, has a “root of 2” ratio. Openings are expressed in micrometers (µm).

For practical purposes, the complete series of sieves is very rarely used, instead only those sizes of importance for the application are used. In any case, the screens are arranged in descending order of opening, placing the screen with the largest mesh opening in the upper part of the apparatus and the screen with the smallest mesh opening in the lower part of the assembly (Cari & Castro, 2014).

After the sieves are correctly prepared for the screening, the process itself consists of passing a mixture of particles of different sizes through the sieves. The smaller particles pass through the holes of the sieve through it and the large ones are retained by it. Screening is a physical method of separating mixtures (Cisa, 2020).

At the beginning of each test, a screening was carried out on the sample to be tested before milling. The objective of this screening was to determine the amount of particles smaller than 45µm that the sample contained. With this data, it was possible to compare this amount of fines before milling with those obtained after milling.

Figure 12: Fines' determination process in the original sample before grinding. On the left there is the coarse greater than 22.4mm and on the right there are the rest of the sizes, still to be separated.

As mentioned previously, the samples contained large pieces that, although irrelevant to check the amount of material with a size smaller than 45µm, could hinder the screening process by preventing the vibratory movement of the sieve set due to their high weight. Therefore, each sample was divided in two for its analogous analysis, but avoiding a saturation of the sieve set.

Following the standardized sequence of sieves with a "root of 2" value, the necessary mesh openings in the sieves to be used were determined. The values obtained were, in micrometers (µm): 65000, 46000, 32000, 22400, 16000, 11200, 8000, 5600, 4000, 2800, 2000, 1400, 1000, 710, 500, 355, 250, 180, 125, 90, 63, 45 and 32. This sieve combination is shown in Figure 13.

Figure 13: Set of sieves used for screening.

Due to the fineness of the particles, part of these remain in the openings of the screens, thus reducing their efficiency. To prevent this problem, ceramic balls (Figure 14) are inserted into each sieve.
A series of tests were carried out to determine the optimal number of balls.
It was concluded that 4 balls were sufficient to avoid agglomeration of particles in the openings.

Figure 14: Ceramic balls on top of the screen to decrease the attachment of the particles through the sieves.

In a similar way, the optimal screening time for the correct passage of the particles through the screening was studied. For screens with a mesh size greater than 500µm the time could be shorter, but for screens with a mesh size lower than this amount the minimum screening time should be about 15 minutes.

### 4.2.5 Evaluation of milling test correction

After its analysis, the sample was stored by the amount retained on each sieve in different plastic bags. With the results, a series of values was calculated: percentage retained, accumulated retained percentage and passing percentage (Table 5). This last value is the one used in the graph that represents a granulometric curve as shown in Figures 16 and 17.

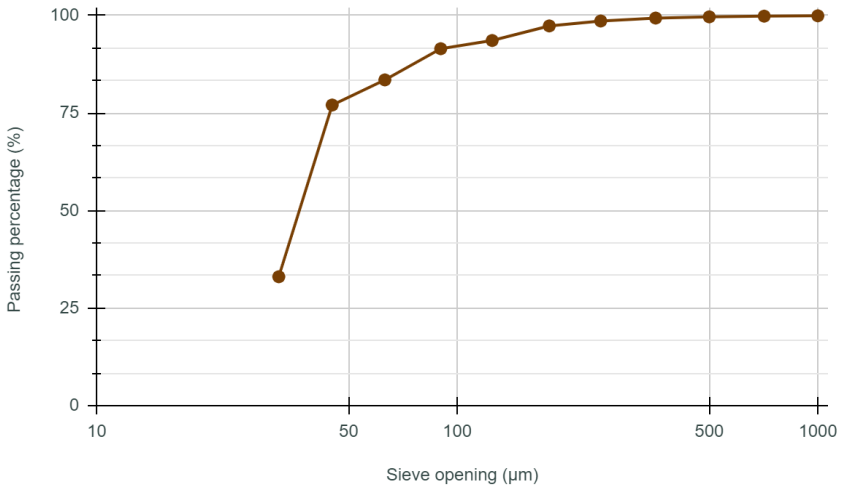


Figure 15: Example of a granulometric curve, using the passing percentage, for sample #13.

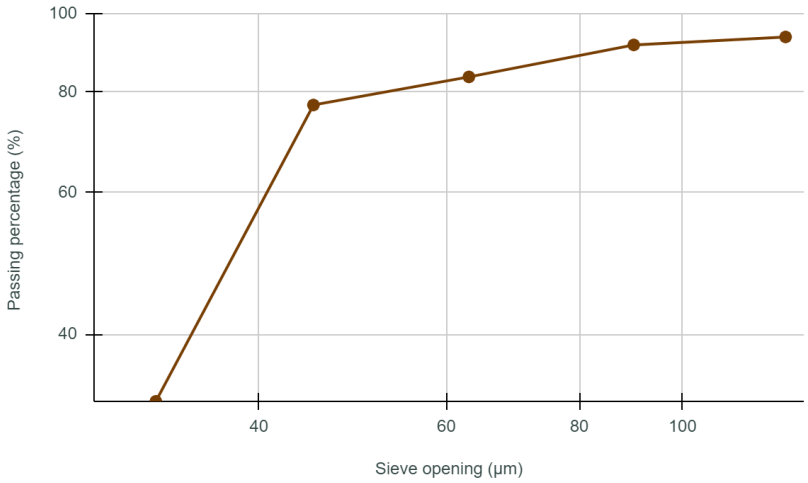


Figure 16: Close-up of the most interesting PSD in sample #13, from 32 to 125µm.

The values obtained and the granulometric curve were studied in search of agglomerations of material by sections, possible causes of inefficient grinding or advances or beneficial options for the purpose of experimentation.

### 4.2.6 Constitution of artificial samples

In order to reach the objective established values of the sample (92-95% of material with a size below 45µm, that is, the percentage passing value) it was decided to manufacture artificial samples combining material from different grinding products. To do this, the characteristics of each test were studied, trying to gather samples that had been ground under conditions as similar as possible (pattern of grinding bodies, grinding time...).

For the preparation of these samples, the Portuguese Standard NP EN 196 "Foundation test methods: determination of mechanical resistance" was followed. According to this standard, the mixture to be made later for the production of the specimens that will be subjected to resistance tests must contain 450g of cement, and therefore samples of approximately 470g were made, leaving a margin for future granulometric analysis and possible loss of material.

The procedure was as follows:

I. Study of the grinding conditions of the samples and grouping among the most appropriate.
II. The pertinent calculations were carried out to know how much material of fines (less than 45µm) each artificial sample should contain, putting as a condition values that were between 92 and 95%, the objective value (Table 9). The remaining sizes were randomly designated to fit the new artificial sample closely to an industrial mill production.

III. Mixing of the samples by particle size. Thus, several samples were joined, for example #3 and #4, particles smaller than 45μm on the one hand, particles larger than 45μm and smaller than 63μm on the other hand, and similarly for the rest, the largest size being between 90-125μm.

IV. Following the aforementioned calculations, the artificial samples were produced.

V. 5g of each artificial sample was removed for the subsequent granulometric study at the Malvern, and another 4g of material to be sent to the supplier company. After this extraction the artificial samples were stored.

Table 9: Composition of the artificial samples.

| Artificial Sample | Mixture of samples | Composition (%) | Particle Size Distribution, PSD | | | | | | | | Total weight (g) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Percentage (%) | | | | Weight (g) | | | | |
| | | | -45μm | -63 +45μm | -90 +63μm | -125 +90μm | -45μm | -63 +45μm | -90 +63μm | -125 +90μm | |
| A | #3+#4 | 93% CK, 7% G | 95 | 3 | 1,2 | 0,8 | 443,3 | 14 | 5,6 | 3,7 | 466,6 |
| B | #5+#7 | 93% CK, 7% G | 95 | 2,25 | 1,75 | 1 | 443,3 | 10,5 | 8,2 | 4,7 | 466,6 |
| C | (#3+#4)+#6+ #8+#10 | 93% CK, 7% G | 93 | 3,2 | 2,5 | 1,3 | 433,9 | 14,9 | 11,7 | 6,1 | 466,6 |
| D | (#3+#4)+#6+ #8+#9+#10 | 93% CK, 7% G | 94 | 2,75 | 2 | 1,25 | 438,6 | 12,8 | 9,3 | 5,8 | 466,6 |
| E | #11+#12+#14 | 93% CK, 7% G | 92 | 3,5 | 2,8 | 1,7 | 432,4 | 16,5 | 13,2 | 8 | 470 |
| F | #11+#12+#14 | 93% CK, 7% G | 93 | 3,7 | 1,8 | 1,5 | 437,1 | 17,4 | 8,5 | 7,1 | 470 |
| G | (#3+#4)+#6+ #8+#9+#10+ #13+#15 | 93% CK, 7% G | 94 | 2 | 2 | 2 | 441,8 | 9,4 | 9,4 | 9,4 | 470 |
| H | (#3+#4)+#6+ #8+#9+#10+ #13+#15 | 93% CK, 7% G | 92 | 3 | 2,5 | 2,5 | 432,4 | 14,1 | 11,8 | 11,8 | 470 |
| I | #16+#17 | 93% CK, 7% G | 93 | 2,75 | 2,5 | 1,75 | 437,1 | 12,93 | 11,75 | 8,23 | 470 |
| J | (#3+#4)+#6+ #8+#9+#10+ #13+#15+#1 6+#17 | 93% CK, 7% G | 91 | 4 | 2,5 | 2,5 | 427,7 | 18,8 | 11,75 | 11,75 | 470 |
| *K* | #19+#21 | 93% CK, 7% G | 92 | 3 | 2.5 | 2.5 | 432.4 | 14.1 | 11.75 | 11.75 | 470 |

More milling was carried out in order to have enough fine material for the manufacture of these artificial samples.

### 4.2.7 Analysis of the granulometry of artificial samples using a laser diffraction test

As referred, for each artificial sample, small subsamples of about 5g each were taken to be tested on the Malvern laser particle analyser. The operation of the analyser is very basic: a sample of the material is expelled through a tube of compressed air and passes through a beam of laser light.

"*Laser diffraction measures particle size distributions by the angular variation of the intensity of scattered light when a laser beam passes through a sample of scattered particles. Large particles scatter light at small angles relative to the laser beam, and small particles scatter light at large angles.*

*The angular scattering intensity data is then analysed to calculate the size of the particles responsible for creating the scattering pattern, using the Mie theory of light scattering. Particle size is recorded as a sphere diameter equivalent to volume*." (Malvern Panalytical, 2021)

The laser diffraction test is a technique recognized by ISO 13320 (2009), consisting of a laser machine (Malvern laser) capable of determining particle size distributions ranging from nanometer to millimeter scale.

Due to the advanced age of the machine (1994), the results could only be consulted on the computer screen itself as seen in Figure 17.

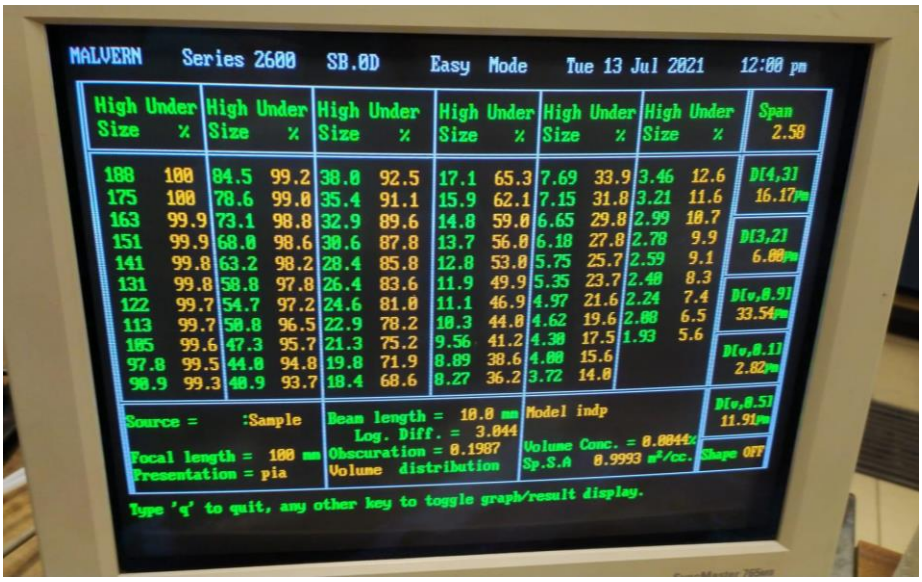


Figure 17: Malvern data obtained in the computer screen (sample I).

Three tests were carried out with the laser analyser for each sample, in order to subsequently average the values. Table 10 shows the main values of these means that have been considered to create the granulometric curve of the artificial samples:

Table 10: Average of the values obtained in the 3 tests performed on the Malvern analyzer per sample, specifying the 3 specific values for particles smaller than 45μm, the target value.

| Sample | PSD by screening | PSD by granulometry laser | | | Average PSD by granulometry laser | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | -45μm (%) | -45μm (%) | | | | | | | | | | |
| | | Test 1 | Test 2 | Test 3 | 10μm | 20μm | 32μm | 45μm | 63μm | 90μm | 125μm | 180μm |
| A | 95 | 94,2 | 92,1 | 95,8 | 41,4 | 73,4 | 90 | 94,03 | 97,1 | 99 | 99,7 | 100 |
| B | 95 | 92,5 | 96,9 | 95,1 | 53,1 | 79,9 | 91,1 | 94,83 | 97,6 | 98,9 | 99,5 | 100 |
| C | 93 | 96 | 95,8 | 96,4 | 45,8 | 76,6 | 91,7 | 96,06 | 98,4 | 99,4 | 99,8 | 100 |
| D | 94 | 94,4 | 94,2 | 94,6 | 51,7 | 80,2 | 91 | 94,4 | 96,7 | 97,9 | 98,8 | 100 |
| E | 92 | 94,5 | 94,6 | 94,9 | 39,5 | 69,3 | 89,2 | 94,66 | 98,4 | 100 | 100 | 100 |
| F | 93 | 93,6 | 94 | 94,8 | 44,9 | 73,1 | 89,1 | 94,13 | 97,8 | 99,6 | 100 | 100 |
| G | 94 | 94,1 | 95,1 | 94,2 | 40,2 | 73,7 | 89,1 | 94,46 | 98,3 | 99,6 | 99,9 | 100 |
| H | 92 | 95,1 | 94,5 | 95,4 | 45,4 | 73,4 | 90 | 95 | 98,6 | 99,6 | 99,9 | 100 |
| I | 93 | 94,7 | 94,1 | 94,8 | 39,5 | 71,4 | 89,3 | 94,53 | 98,1 | 99,4 | 99,8 | 100 |

### 4.2.8 Manufacture of mortar specimens

With the particle size distribution of the samples conducted according to pre-established values, the preparation of mortar specimens was made for the study of the compressive resistance.

The granulometric curves of the samples were studied, being samples A, B, D, G, and I of special interest. The reason for choosing these samples is found in the difference observed between two groups of samples; on the one hand B and D, with a percentage of particles of size equal to or less than 10μm of values 53.1% and 51.7%, and on the other hand group A, G and I, with percentages of 41.4%, 40.2% and 39.5% respectively.

According to the standard NP EN 196- 1, each mix has to contain 450g of cement, 1350g of CEN standardized sand and 225g of water, resulting in 3 specimens for each mix produced.

The procedure for mixing materials was as follows:

I. Mixing the cement with water in the programmable automatic mixer AUTOMIX (Figure 18).
II. The procedure was established as it is indicated in the NP EN 196-1.


Figure 18: Programmable automatic mixer AUTOMIX.

With the mortar mixture ready, it was proceeded to study its workability. To do this, a fluidity test was carried out, which consists of introducing part of the mixture into a hollow, truncated conical container, placing this container in the center of a shaking table, removing the container leaving only the mixture on the table, and then subject the table to a series of sudden falls by means of a crank following the UNE-EN 1015-3. The diameter of the mixture is then measured, which is clearly expanded compared to its initial state (Figure 19).

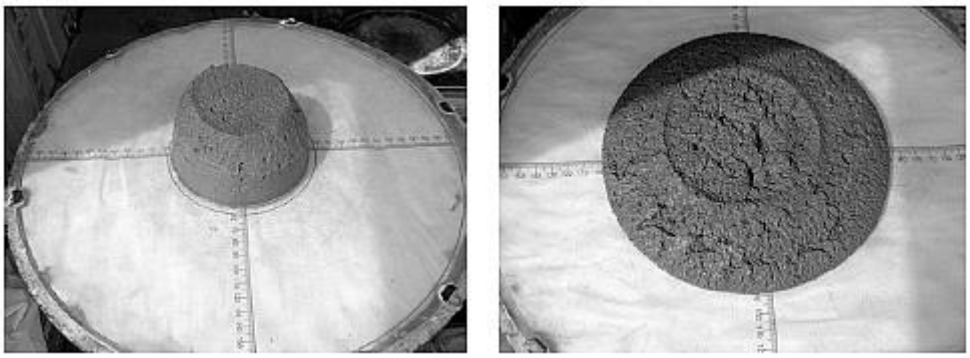

Figure 19: Specimen before and after the procedure of the fluidity test (Construmática, 2018).

The next step consists of the settlement of the mixture in the molds for the formation of the 3 specimens. For this, a compactor was used (Figure 20), a machine that performs vertical shaking of the mold in order to fill gaps, eliminate air cavities and evenly distribute the mixture in the mold. According to the NP EN 196-1 standard, for compressive strength tests, 60 shocks must be carried out on the compactor.

Figure 20: Compactor machine loaded with a 3-specimen mold.

Subsequently, the mold is removed from the machine, the excess material is removed and cleaned, and it is identified by means of labels for storage in a humid chamber during the 2, 7 and 28 days of curing time that were established for this experimentation.

As there were 3 specimens per sample, each one had a different cure time; one of them healed in the chamber for 2 days, another for 7 days and another for 28 days. The cure chamber is characterized for having a temperature of approximately 20 ± 2 °C and a relative humidity of 95 ± 5%.

### 4.2.9 Bending and compression resistance tests on the specimens

After the curing time determined by the standard, tensile tests were performed first and then compression tests on each of the specimens.

A bifunctional press was used to perform these tests. The procedure was as follows:

#### 4.2.9.1 Tensile test

I. Place the specimen in the tension press and start the approximation of it until the specimen-press contact is made.
II. Start the process and control the speed of the press until it is set at the desired value.
III. Wait for the specimen to break (Figure 21) and note the breaking stress.
IV. Open the press to be able to remove the two halves of the test tube and reserve momentarily until the compression test performance.

Figure 21: Image of the tensile test being carried out.

#### 4.2.9.2 Compression test

I. Place one of the halves obtained from the previous test in the compression press and start the approximation of this until it makes contact with the specimen-press.

II. Start the process and control the speed of the press until this constant is set at the desired value (i.e. speed requirements are established in the standard). Wait for the specimen to break (Figure 22) and register the breaking stress.

III. Open the press to be able to remove the specimen and repeat the process with the other remaining half.

Figure 22: Image of the compression test being carried out.

## 5. Results

This section will comment on the results obtained, both in the manufacturing process of the samples and in their testing.

Trials #1 and #2 will be avoided in all the ensuing discussion of results. The first is due to its wrong composition, since it does not conform to the parameters subsequently established by the cement company CIMPOR. The second trial was ruled out due to a failure in handling the sample.

For the evaluation of the results, attention is paid to the values obtained in the two most relevant stages of the experimentation (preliminary tests and resistance tests). These values are compared with each other on the grounds of cause.

As described in the introduction to this study, a specific fine range and high compressive strength are sought.

### 5.1 Results observed in the constitution of the samples

It is important to make an incursion into the results obtained in the process of grinding and manufacturing the cement samples to understand the part that forms the basis of this project. It is also important to always keep in mind the conditions (i.e. variable parameters, Table 11) that shaped this experiment from the beginning.

Table 11: Parameters according to their condition of constancy or variability in the experiment.

| Constant parameters | Variable parameters |
|---|---|
| Speed rotation (rpm) | Milling time |
| | Body load pattern |
| | Grinding aid |
| Feed mass | Pre-milling of clinker |
| | Pre-milling of gypsum |

The data obtained in the constitution of the samples is shown in Figure 23 and Table 12. This data is described in the following paragraphs. The values of the passing percentage and final residue are collected in a comparative way between the initial samples in Figure 22. They are also written in Table 9 where its relationship with the experimentation conditions can be appreciated.

As it can be seen in the table, it is not until test #8 and #9 were significant advance if made in order to reduce the final residue percentage, being approximately 25,5% and 22% respectively. All tests include a pre-grinding of gypsum.

In the case of test #9 one drop of additive (MAGA C077, supplier MAPEI) was added to prevent fine cement particles from sticking in the cavity of the mill. Pre-grinding of clinker is carried out to facilitate grinding.
In the next sample used, #10a and #10b, it is tested in the same sample how time affects the fineness of the particles. The results show there is a minimal difference in the final residue for a 30 mins gap in between the mills, being those values 26% and 27.5% respectively.
The same happens with tests #12a and #12b, where the time difference is 60 mins from 120 to 180 mins and the values of the final residue show a minimal difference.
It is decided at this point to design a third grinding load pattern that results in a midpoint between pattern 1 and 2 in terms of the number of balls of different sizes, keeping the total mass of the balls constant (Table 8).
In test #11, a new body load pattern is experimented, maintaining the conditions set before. The results are very similar to those obtained in the last tests, with a 25.03% final residue.

At this point and against the values resulting from each test, it is determined that the most favourable grinding conditions are those set for test #9 (plus adding double additive):

I. Carry out a pre-milling of both the gypsum and the clinker.
II. Add two drops of additive to the mill.
III. Keep the grinding time at 120 minutes.
IV. Use grinding body pattern number 1.

Additionally, in Table 12 the initial milling conditions for the preliminary tests and the commented results can be observed. It should be noted that a pre-milling of the gypsum was carried out in every test, so since it is a constant and not a variable it does not appear on Table 12. The tables regarding the data used to elaborate Table 12 are found in annexes.

Table 12: Initial conditions and results in milling tests.

| *Test sample #* | TEST CONDITIONS | | | | | | | | | | RESULTS | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Composition | Pre-milling of CK | Grinding aid (drops) | Total weight (g) | Coarse >45µm (g) | Fine <45µm (g) | Loss (g) | Initial residue (%) | Milling body load | Milling time (mins) | D50 (µm) | D80 (µm) | D90 (µm) | Passing percentage (%) | Final residue (%) |
| 3 | 93% CK, 7% G | | | 466,6 | 461,8 | 4,2 | 0,6 | 98,97 | 1 | 60 | 0 | 120 | 250 | 52,55 | 47,45 |
| 4 | 93% CK, 7% G | | | 466,6 | 462,9 | 2,9 | 0,8 | 99,21 | 2 | 55 | 0 | 90 | 200 | 63,87 | 36,13 |
| 5 | 93% CK, 7% G | | | 467,7 | 461,3 | 5,7 | 0,7 | 98,63 | 2 | 55 | 55 | 180 | >500 | 33,16 | 66,84 |
| 6 | 93% CK, 7% G | | | 466,8 | 456,6 | 7,5 | 2,7 | 97,81 | 2 | 120 | 68 | 105 | 250 | 3,91 | 96,09 |
| 7 | 93% CK, 7% G | | | 466,8 | 463,5 | 1,6 | 1,7 | 99,66 | 1 | 120 | 0 | 32 | 180 | 69,01 | 30,99 |
| 8 | 93% CK, 7% G | | | 466,7 | 462,3 | 4,4 | 0,8 | 99,28 | 1 | 120 | 0 | 35 | 125 | 74,53 | 25,47 |
| 9 | 93% CK, 7% G | ✓ | 1 | 466,5 | 457,8 | 7,5 | 1,2 | 98,14 | 1 | 120 | 0 | 50 | 95 | 77,76 | 22,24 |
| 10a | 93% CK, 7% G | ✓ | 1 | 466,9 | 457,8 | 8,7 | 0,4 | 98,05 | 2 | 120 | 0 | 60 | 120 | 73,73 | 26,27 |
| 10b | 93% CK, 7% G | ✓ | 1 | 466,9 | 457,8 | 8,7 | 0,4 | 98,05 | 2 | 150 | 0 | 65 | 145 | 72,48 | 27,52 |
| 11 | 93% CK, 7% G | ✓ | 1 | 466,9 | 454,7 | 12,2 | 0,8 | 97,55 | 3 | 120 | 0 | 55 | 100 | 74,97 | 25,03 |
| 12a | 93% CK, 7% G | ✓ | 2 | 466,8 | - | - | - | 98,57 | 1 | 120 | 0 | 50 | 110 | 76,31 | 23,69 |
| 12b | 93% CK, 7% G | ✓ | 2 | 466,8 | - | - | - | 98,57 | 1 | 180 | 0 | 55 | 125 | 75,39 | 24,61 |
| 13 | 93% CK, 7% G | ✓ | 2 | 466,8 | - | - | - | 98,57 | 1 | 120 | 0 | 50 | 75 | 77,04 | 22,96 |

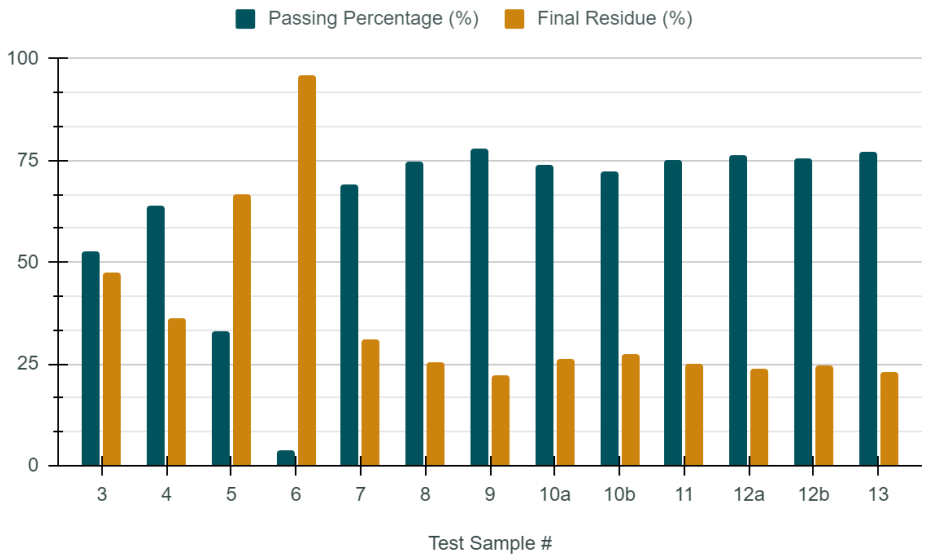


Figure 23: Comparative graph between the passing percentage and the final residue of the initial samples.

## 5.2 Granulometry analysis of the milled product

The analysis carried out on the artificial samples in the laser granulometry was performed to have some comparison values with the values obtained in the screening for the percentage of particles -45µm. Table 13 shows the values obtained in each measure and the average value as well as the standard deviation for each sample. The variation between the values obtained for this particle size was studied using the standard deviation formula since:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n}} \quad (1)$$

Being $x$ a set of numbers and therefore $xi$ each of the values of the data, $\bar{x}$ is the average of this set of numbers and $n$ is the number of the data points.

Standard deviation is a measure used to quantify the spread or variation of a set of numerical data. If, when calculating the standard deviation, a low value is obtained, it is indicating that most of the numerical data of the analyzed set are in an environment close to the mean of said data, while a high standard deviation value indicates that the data is distributed over a wider range of values (Valero, 2013)

Figure 24 shows a comparison between the 3 measured values in each analysis and the average values obtained.

Table 13: Values obtained for the standard deviation in each of the samples subjected to granulometric analysis by means of the MALVERN.

| Sample | PSD by granulometry laser -45µm (%) | | | Test Average (%) | Standard Deviation |
|---|---|---|---|---|---|
| | Test 1 | Test 2 | Test 3 | | |
| A | 94,2 | 92,1 | 95,8 | 94,03 | 1,52 |
| B | 92,5 | 96,9 | 95,1 | 94,83 | 1,81 |
| C | 96 | 95,8 | 96,4 | 96,01 | 0,25 |
| D | 94,4 | 94,2 | 94,6 | 94,4 | 0,2 |
| E | 94,5 | 94,6 | 94,9 | 94,67 | 0,17 |
| F | 93,6 | 94 | 94,8 | 94,13 | 0,5 |
| G | 94,1 | 95,1 | 94,2 | 94,47 | 0,45 |
| H | 95,1 | 94,5 | 95,4 | 95 | 0,37 |
| I | 94,7 | 94,1 | 94,8 | 94,53 | 0,31 |

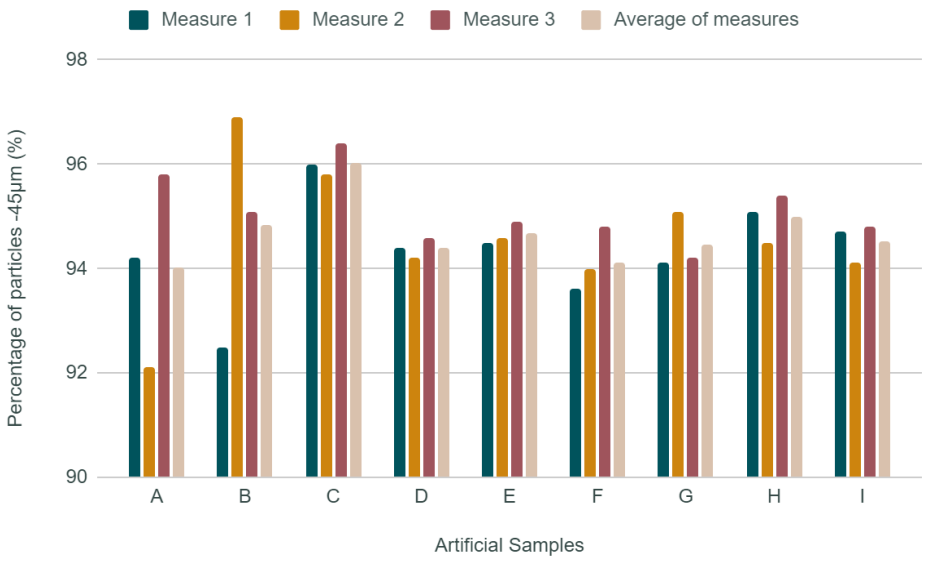


Figure 24: Comparative graph between the values obtained in the individual measurements and the mean of these values.

Standard deviation is a measure used to quantify the spread or variation of a set of numerical data. If, when calculating the standard deviation, a low value is obtained, it is indicating that most of the numerical data of the analyzed set are in an environment close to the mean of said data, while a high standard deviation value indicates that the data is distributed over a wider range of values.

Since the obtained standard deviation values are very low, it can be said that the variation between the 3 granulometric analyses made with the MALVERN of the artificial samples is minimal, and therefore the data obtained in said analyzes are reliable.

Due to the lack of availability of the MALVERN in the last stage of the laboratory, and how the low standard deviation found in the tests shown so far has been commented on, in samples #J and #K only the granulometric analysis by screening was carried out.

For the manufacture of the specimens, the PSD of the samples obtained in the MALVERN was taken into account. Special interest was paid to the percentages of finer particles, 10µm, to study their possible effect on compressive strength. Table 14 shows the values obtained in the MALVERN that were used for grouping the samples into 3 subsequent groups.

These above-mentioned groups were formed by joining together samples with similar values for the size of 10µm.

Table 14: Values obtained from the MALVERN analysis. *Values obtained for particles -45µm by screening.

| Artificial Sample | Average PSD by granulometry laser | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 10µm | 20µm | 32µm | 45µm | 63µm | 90µm | 125µm | 180µm |
| A | 41,4 | 73,4 | 90 | 94,03 | 97,1 | 99 | 99,7 | 100 |
| B | 53,1 | 79,9 | 91,1 | 94,83 | 97,6 | 98,9 | 99,5 | 100 |
| C | 45,8 | 76,6 | 91,7 | 96,06 | 98,4 | 99,4 | 99,8 | 100 |
| D | 51,7 | 80,2 | 91 | 94,4 | 96,7 | 97,9 | 98,8 | 100 |
| E | 39,5 | 69,3 | 89,2 | 94,66 | 98,4 | 100 | 100 | 100 |
| F | 44,9 | 73,1 | 89,1 | 94,13 | 97,8 | 99,6 | 100 | 100 |
| G | 40,2 | 73,7 | 89,1 | 94,46 | 98,3 | 99,6 | 99,9 | 100 |
| H | 45,4 | 73,4 | 90 | 95 | 98,6 | 99,6 | 99,9 | 100 |
| I | 39,5 | 71,4 | 89,3 | 94,53 | 98,1 | 99,4 | 99,8 | 100 |
| J | | | | 91* | | | | |
| K | | | | 92* | | | | |

## 5.3 Results of the compression tests

The compression tests were carried out following the NP EN 196-1 standard for conducting tests on cement specimens.

The results obtained were processed and the bending and compression strengths were calculated following the formulas established in the standard itself and mentioned below:

$$R_f = \frac{1{,}5\ x\ F_f\ x\ l}{b^3} \qquad (2)$$

Being $Rf$ the flexural strength in megapascals, $b$ is the side of the prism's square section, in millimeters, $Ff$ is the load applied to the center of the prism at break in newtons, and $ll$ is the distance between supports in millimeters.

$$R_c = \frac{F_c}{1600} \qquad (3)$$

Where $Rc$ is the compressive strength in megapascals, $Fc$ is the maximum breaking load in newtons and $1600$ is the area of the plates or auxiliary plates (40mm x 40mm) in square millimeters.

Tables 15a, 15b and 15c show the values obtained in each test, both for flexion and compression, having two values in the latter category since, due to the nature of the flexural test, two compression test pieces were obtained.

In Figure 25 the calculated values of compressive strength are shown in a comparative way.

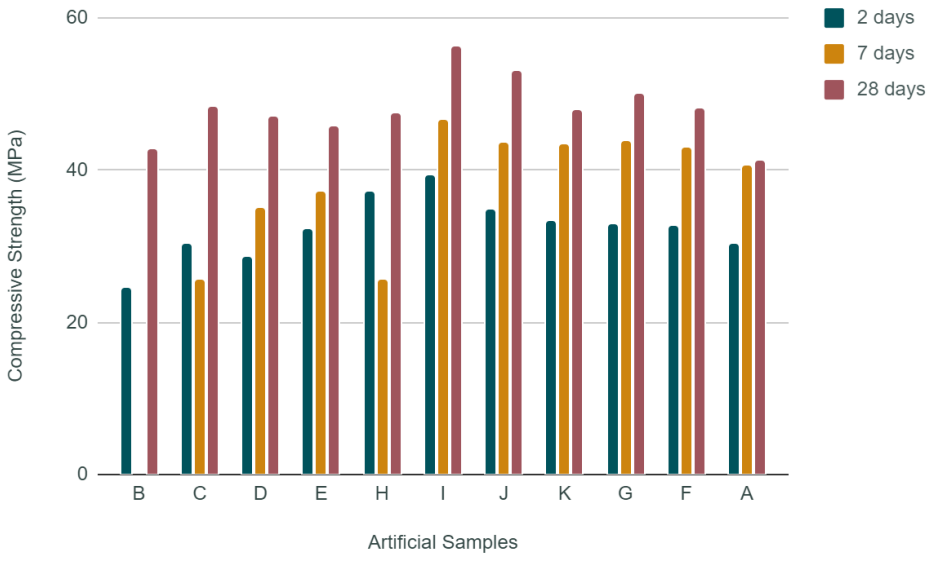


Figure 25: Compressive strength obtained in the tests with different percentages of fine particles below 45µm and different curing times.

Table 15a: Results obtained in bending and compression tests with the values calculated from formulas (1) and (2) and with a healing time of 2 days.

2 DAYS

| Sample | Workability (mm) | Weight (g) | Tensile stress (N) | Tensile strength (MPa) | Compressive stress (N) (1) | Compressive stress (N) (2) | Compressive strength (MPa) |
|---|---|---|---|---|---|---|---|
| B | 224,52 - 224,43 | 562,4 | 2234 | 5,24 | 50020 | 28210* | 24,45 |
| D | 224,8 - 224,52 | 591,3 | 2238 | 5,25 | 44010 | 47510 | 28,6 |
| C | 213,51 - 213,47 | 580,3 | 2352 | 5,51 | 35200 | 48450** | 30,28 |
| H | 200,30 - 198,23 | 607,3 | 2863 | 6,71 | 60590 | 58660 | 37,27 |
| F | 202,19 - 202,20 | 594 | 2975 | 6,97 | 51440 | 53080 | 32,66 |
| A | 231,47 - 233,10 | 591,2 | 2064 | 4,84 | 49320 | 47880 | 30,38 |
| G | 206,78 - 206,08 | 591,1 | 2201 | 5,16 | 51080 | 54080 | 32,86 |
| I | 201,56 - 201,2 | 600,8 | 2837 | 6,65 | 66200 | 59400 | 39,25 |
| J | 225,45 - 226,20 | 597,2 | 2746 | 6,44 | 55740 | 55580 | 34,79 |
| E | 208,19 - 208,2 | 586 | 2537 | 5,97 | 50350 | 53150 | 32,34 |
| K | 243,19 - 239,71 | 597,6 | 2738 | 6,42 | 52830 | 53560 | 33,25 |

Table 15b: Results obtained in bending and compression tests with the values calculated from formulas (1) and (2) and with a healing time of 7 days.

7 DAYS

| Sample | Weight (g) | Tensile stress (N) | Tensile strength (MPa) | Compressive stress (N) (1) | Compressive stress (N) (2) | Compressive strength (MPa) |
|---|---|---|---|---|---|---|
| B | 565,6 | - | - | - | - | - |
| D | 590,1 | 2473 | 5,80 | 53310 | 58980 | 35,09 |
| C | 579,3 | 2511 | 5,89 | 50710 | 31230 | 25,61 |
| H | 593,7 | 2808 | 6,58 | 38180 | 43790 | 25,62 |
| F | 575,8 | 2798 | 6,56 | 70220 | 67450 | 43,02 |
| A | 569,4 | 2676 | 6,27 | 65830 | 64090 | 40,60 |
| G | 569,1 | 2639 | 6,19 | 72020 | 68470 | 43,90 |
| I | 616,2 | 2788 | 6,53 | 76710 | 72730 | 46,70 |
| J | 572,3 | 2517 | 5,90 | 67630 | 72070 | 43,66 |
| E | 585,6 | 2579 | 6,04 | 58550 | 60580 | 37,23 |
| K | 546,2 | 2749 | 6,44 | 67480 | 71410 | 43,40 |

Table 15c: Results obtained in bending and compression tests with the values calculated from formulas (1) and (2) and with a healing time of 28 days.

28 DAYS

| Sample | Weight (g) | Tensile stress (N) | Tensile strength (MPa) | Compressive stress (N) (1) | Compressive stress (N) (2) | Compressive strength (MPa) |
|---|---|---|---|---|---|---|
| **B** | 547,3 | 2643 | 6,19 | 71430 | 65320 | 42,73 |
| **D** | 569,4 | 3000 | 7,03 | 72470 | 78270 | 47,11 |
| **C** | 569 | 2801 | 6,56 | 78550 | 76240 | 48,37 |
| **H** | 589,8 | 2935 | 6,88 | 80330 | 71740 | 47,52 |
| **F** | 601,4 | 2895 | 6,79 | 74840 | 78870 | 48,03 |
| **A** | 591,45 | 2925 | 6,86 | 72000 | 59890 | 41,22 |
| **G** | 594,75 | 2895 | 6,79 | 80470 | 79.410 | 49,96 |
| **I** | 593,2 | 2572 | 6,03 | 92490 | 87710 | 56,31 |
| **J** | 596,85 | 2993 | 7,01 | 86880 | 82990 | 53,08 |
| **E** | 564,6 | 2738 | 6,42 | 74780 | 71850 | 45,82 |
| **K** | 597,4 | 2902 | 6,80 | 75460 | 77670 | 47,85 |

Along general lines and as can be seen in Figure 24, the calculated compressive strength of each specimen increases in value with the passage of time in the curing chamber.

In Tables 15a, 15b and 15c these variations can be observed in a more numerical way. This is where this section will focus to analyse these fluctuations and possible relationships.

There is a common denominator for the samples that have been shown to be the best in terms of greater resistance to compression presented; they are the ones with the best resistance at all times (2, 7 and 28 days). These samples are G, I and J. In particular, sample I presents a resistance much higher than the others from the first test, with a value of 39.25MPa after 2 days of cure, and a value of 56.31MPa in the test at 28 days. On the other side is the specimen with the worst results, A, with 30.38MPa at 2 days of curing and 41.22MPa at 28 days. The difference between these specimens is almost 9MPa in the case of the first test and more than 15MPa in the third. But both specimens follow the same behavior regardless of whether they are more or less resistant: both have proven in all tests to be the best and the worst specimen. Observing more particularities of the specimens I and A, it can be seen that I has an "average" amount of particles -45µm, 93%, compared to A that has the maximum number of particles of this size among all the specimens, 95%. In the next chapter, the composition according to the particle size and its relationship with the obtained compressive strength values will be discussed.

The constant evolutionary behavior of the specimens is also repeated in the others. For example, the specimens F and K show a similar evolution in all the tests carried out on them. An exception to this rule is test tube D, which despite having a very low result in its first test, manages to position itself among the most prosperous samples with 47.11MPa in its final test.

In order to facilitate the treatment of the specimens, they have been classified into better specimens, intermediate specimens and worse specimen. In this way, in the first group, G, I and J would be found as mentioned, in the second group C, F, K, HD and E, and in the third only A. In the discussion, the best specimens will mainly be discussed, but some peculiarities of the rest will also be analysed.
It should be noted that test tube B has been discarded in the observation and analysis of results since it suffered a composition alteration in the mixer at the time of its elaboration.

# 6. Discussion

The relationships and behaviors observed between variables of the experimentation are discussed below, as well as comparisons with other experiments or unusual traits, in order to formulate final conclusions and establish recommended future fields of research.

The values obtained in chapter 5 “Results” will be discussed in relation to other studies carried out to date, as well as the similarities or differences between them.

## 6.1 Discussion about the constitution of the samples

It is known that ball pattern, milling method and feed materials directly influence the PSD obtained in the product after milling.

In 2006 Binici et al. confirmed through their experiment the influence of one of these variables: the milling method used. After interpreting the data from their experimentation, they conclude that milling efficiency (greater production of fine particles) is higher in a milling method where the materials that make up the compound are ground separately and then brought together than when the materials are ground all together.

In the case of this study, a variable to take into account to achieve a lower PSD could have been the performance of tests where the clinker was ground on one side and the gypsum on the other.
Taking into account that the purpose of this experiment is based on an energy efficiency basis in the milling phase, that is, a reduced electrical energy consumption as far as possible, the separate milling method may not be the one more suitable for this purpose, since the consumption of electrical energy is lower when the elements of a composite are milled simultaneously.

Of course, directly related to the grinding time, is the electrical consumption required by the mill. This is the main reason why leaving the mill on indefinitely until obtaining the desired product is not feasible. In addition, as discussed in subchapter 5.1, it is observed in tests #10a and #10b, as well as in tests #12a and #12b, that by increasing the milling time in the same sample, the improvement in the reduction of the size of the material is very small, negligible compared to the consumption exerted by the mill at that time.

Regarding the pattern of balls used, it is Ghalandari and Iranmanesh who, in 2020, carry out an experiment in which, as in this experiment, they vary the sequence of the loading of milling bodies. In their case, they do so because the surface area of the balls in their pattern is below the design ball charge stipulated for their mill (28.5m2/ton versus 33.1m2/ton respectively). In their article they confirm that increasing the surface area of the ball pattern improves the performance of the mill and is permissible as long as this increase does not lead to a reduction in the crushing force; in the event that this parameter is reduced excessively, the efficiency of the mill would decrease.

Extrapolating this question to this study, it can be seen that the same premise is fulfilled; the most efficient ball pattern is 1, and it is also the one with the highest contact surface area (Table 16). Although the difference between the standards is small, it would have been an option to increase the difference in surface area of the standards to a greater extent to be able to see if it was a beneficial change in order to obtain the desired PSD.

Table 16: Surface area of the body load patterns.

| Ball diameter (m) | Surface area per ball (m²) | 1 | | 2 | | 3 | |
|---|---|---|---|---|---|---|---|
| | | Number of balls | Surface area per ball size (m²) | Number of balls | Surface area per ball size (m²) | Number of balls | Surface area per ball size (m²) |
| 0,048 | 0,0072 | 4 | 0,0288 | 7 | 0,0504 | 5 | 0,036 |
| 0,04 | 0,005 | 14 | 0,07 | 17 | 0,085 | 15 | 0,075 |
| 0,03 | 0,0028 | 28 | 0,0784 | 16 | 0,0448 | 22 | 0,0616 |
| 0,025 | 0,002 | 4 | 0,008 | 7 | 0,014 | 6 | 0,012 |
| 0,023 | 0,0017 | - | - | 9 | 0,0153 | 15 | 0,0255 |
| 0,019 | 0,0011 | 19 | 0,0209 | - | - | - | - |
| 0,0135 | 0,00057 | 37 | 0,02109 | 11 | 0,00627 | 28 | 0,01596 |
| **Total surface area (m²)** | | | 0,22719 | | 0,21577 | | 0,22606 |
| **Total weight (g)** | | | 9060,51 | | 9059,7 | | 9063 |
| **Total surface area per ton (m²/ton)** | | | **25,07** | | **23,81** | | **24,94** |

## 6.2 Relationships found between the PSD observed in the samples and the compressive strength obtained in the tests

This section will deal with the influence found between the amount of particles of a certain size that make up a cement and the relationship it maintains with the compressive strength measured in the specimens.

In the article by Kim (2017) a relevant question is stated in relation to this research;

In general, it is stated that a low FMC (the fineness modulus, in this particular case of cement, is the sum of the cumulative percentages retained on each sieve and divided by 100) helps to reduce the size of the cement particles, which turns out to be positive to increase the value of the initial force. In the case where the FMC has a high value, this fact is advantageous to reduce the heat of hydration.

On the other hand, in the article by Sajedi and Razak (2011) reported that “the surface area of cement particles was associated with strength development and hydration”. This statement shows that the rate

of hydration depends on the fineness of cement particles, and high fineness was required for a rapid development of strength.

Both articles leave a confirmed precedent that the PSD of the cement directly influences the compressive strength finally found.
When looking at the data obtained from all the experimental tests, it is easy to realize that also on this occasion different resistance values are obtained for different specimens of different size compositions.

The experiment carried out by Ghalandari and Iranmanesh in 2020 provides recent information on the milling of clinker and gypsum in a ball mill in terms of the manner that PSD affects compressive strength. The results they obtain are not very positive regarding PSD. It obtains 9.5% of particles larger than 2mm while only 48% of the material has a size smaller than 90μm. Within this percentage of less than 90μm, only 51% of the particles are between 45-4.5μm. Both authors say that the component particles of cement that have a size greater than 60μm provide a “filling effect”, so they do not really contribute to the development of compressive strength. On the other hand, particles smaller than 3μm “can cause higher early compressive strengths, but also can lead to some problems during the setting time, like unfavorable volume variations and decline in rheological properties”.

Following the results of Ghalandari and Iranmanesh, the quantity of particles smaller and larger than 60μm present in the specimens is analyzed. Taking a look at Table 14, it can be seen that within the group of the best specimens (G, I and J) and compared to the rest there is no notable difference or pattern in terms of the percentage of particles -63 + 45μm. Comparing the best result of test piece I with the worst result of test piece A (in terms of resistance to compression), it can be seen that in the particle size between -90 + 63μm, it is I together with the samples that follow it in values, the one that have the greatest amount of particles in this size, and is A, the specimen that by far has the least amount of these particles. If we look at the following size range, -125 + 90μm, it can be seen that the same dynamics occurs.

In the aforementioned article by Kim (2017) it is stated that “it is generally agreed that cement particles larger than 45μm are difficult to hydrate and those larger than 75μm could never hydrate completely”. Perhaps these particles influence compressive strength in a different way as well as hydration.

## 7. Conclusions and future work

Bearing in mind that the objective of this experimentation is to test experimentally the relationship that the PSD of the ground cement has with the compressive strength shown by the manufactured mortar specimens, always from an energy efficiency point of view in the mixing phase, some statements are concluded with the results and their analysis established:

1. The energy efficiency of the milling process depends on several parameters; grinding time, ball loading pattern, additives for the reduction of caked material on the mill walls and particle size in the input feed. By altering these parameters, a more efficient and functional system can be achieved for a specific objective.
2. Variable time shows no significant improvement in grinding efficiency after a certain number of minutes (120 minutes). Likewise, it has been shown that the ball loading pattern that has worked best has been the one with the largest surface area (pattern 1). In addition, it has been seen in the results that a pre-grinding of the feed material has a positive influence on the PSD obtained, that is, if the feed has a smaller maximum size, the reduction of particle size in the grinding increases.
3. In the laboratory conditions followed, it has not been possible to reduce more than 77.04% of the total feed to a size smaller than 45μm, so new experiments with different variables or industrial conditions are necessary in this regard.
4. The tested specimens follow the same variation regardless of whether their compressive strength is high or low: they evolve towards greater compressive strength as the curing time passes, but they remain stable in terms of their position, that is, the specimen that has shown better results from the beginning always keeps the best and vice versa with the worst.
5. The rapidity of the increase in compressive strength with curing time, so that it is confirmed that the presence of fine particles in the cement improves the speed with which a mortar specimen increases its compressive strength.
6. The specimens that have turned out to be the most resistant to compression are those that, in proportion to all the others, have a higher percentage of particles that varies between 63 and 125μm. On the contrary, the worst result is presented by the specimen with the least percentage of particles in this range.

Several research fields are left open that could open the doors to new information regarding the subject of this study and that have not been included:

1. The influence of the size of the mill chamber on the impact force of the grinding bodies on the feed. Due to the laboratory nature of this experimentation, it has not been tested in real industrial conditions, which could modify, or even improve, the efficiency in reducing the size of the milling phase.
2. In relation to the article written by Ghalandari and Iranmanesh in 2020 that states that cement particles with a size greater than 60μm only cause a “filling effect”, it would be interesting to study the compressive strength in specimens that are manufactured with a cement whose PSD maximum is 60μm. In this experimentation, the maximum PSD has been 125μm, following a

"random" laboratory formulation (in order to simulate a non-artificial grinding) in the mixture of this size with the target size of 45μm.

3. Due to the good results obtained regarding the pre-milling of the feed material, an investigation is suggested on a circuit in which the pre-milling and milling are put sequentially.

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## Annexed Section

Appendix 1: European standards for cement produced in the EU-27 (Schorcht et al., 2013).

| Main types | Notation of the 27 products (types of common cement) | | Composition (percentage by mass([1])) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Main constituents | | | | | | | | | | Minor Additional constituents |
| | | | Clinker | Blast Furnace Slag | Silica Fume | Pozzolana | | Fly ash | | Burnt shale | Limestone | | |
| | | | | | | Natural | Natural Calcined | Siliceous | Calcareous | | | | |
| | | | K | S | D([2]) | P | Q | V | W | T | L([3]) | LL([4]) | |
| CEM I | Portland cement | CEM I | 95–100 | - | - | - | - | - | - | - | - | - | 0–5 |
| CEM II | Portland-slag cement | CEM II/A-S | 80–95 | 6–20 | - | - | - | - | - | - | - | - | 0–5 |
| | | CEM II/B-S | 65–79 | 21–35 | - | - | - | - | - | - | - | - | 0–5 |
| | Portland-silica fume cement | CEM II/A-D | 90–94 | - | 6–10 | - | - | - | - | - | - | - | 0–5 |
| | Portland–pozzolana cement | CEM II/A-P | 80–94 | - | - | 6–20 | - | - | - | - | - | - | 0–5 |
| | | CEM II/B-P | 65–79 | - | - | 21–35 | - | - | - | - | - | - | 0–5 |
| | | CEM II/A-Q | 80–94 | - | - | - | 6–20 | - | - | - | - | - | 0–5 |
| | | CEM II/B-Q | 65–79 | - | - | - | 21–35 | - | - | - | - | - | 0–5 |
| | Portland-fly ash cement | CEM II/A-V | 80–94 | - | - | - | | 6–20 | - | - | - | - | 0–5 |
| | | CEM II/B-V | 65–79 | - | - | - | - | 21–35 | - | - | - | - | 0–5 |
| | | CEM II/A-W | 80–94 | - | - | - | - | - | 6–20 | - | - | - | 0–5 |
| | | CEM II/B-W | 65–79 | - | - | - | - | - | 21–35 | - | - | - | 0–5 |
| | Portland-burnt shale | CEM II/A-T | 80–94 | - | - | - | - | - | - | 6–20 | - | - | 0–5 |
| | | CEM II/B-T | 65–79 | - | - | - | - | - | - | 21–35 | - | - | 0–5 |
| | Portland–limestone cement | CEM II/A-L | 80–94 | - | - | - | - | - | - | - | 6–20 | - | 0–5 |
| | | CEM II/B-L | 65–79 | - | - | - | - | - | - | - | 21–35 | - | 0–5 |

| Main types | Notation of the 27 products (types of common cement) | | Composition (percentage by mass([1])) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Main constituents | | | | | | | | | | Minor Additional constituents |
| | | | Clinker | Blast Furnace Slag | Silica Fume | Pozzolana | | Fly ash | | Burnt shale | Limestone | | |
| | | | | | | Natural | Natural Calcined | Siliceous | Calcareous | | | | |
| | | | K | S | D([2]) | P | Q | V | W | T | L([3]) | LL([4]) | |
| | | CEM II/A-LL | 80–94 | - | - | - | - | - | - | - | - | 6–20 | 0–5 |
| | | CEM II/B-LL | 65–79 | - | - | - | - | - | - | - | - | 21–35 | 0–5 |
| | Portland-composite cement | CEM II/A-M | 80–94 | 6–20 | | | | | | | | | 0–5 |
| | | CEM II/B-M | 65–79 | 21–35 | | | | | | | | | 0–5 |
| CEM III | Blast furnace cement | CEM III/A | 35–64 | 36–65 | - | - | - | - | - | - | - | - | 0–5 |
| | | CEM III/B | 20–34 | 66–80 | - | - | - | - | - | - | - | - | 0–5 |
| | | CEM III/C | 5–19 | 81–95 | - | - | - | - | - | - | - | - | 0–5 |
| CEM IV | Pozzolanic cement([5]) | CEM IV/A | 65–89 | - | 11–35 | | | | | - | - | - | 0–5 |
| | | CEM IV/B | 45–64 | - | 36–55 | | | | | - | - | - | 0–5 |
| CEM V | Composite cement([5]) | CEM V/A | 40–64 | 18–30 | - | 18–30 | | | - | - | - | - | 0–5 |
| | | CEM V/B | 20–38 | 31–50 | - | 31–50 | | | - | - | - | - | 0–5 |

([1]) The values in this table refer to the sum of the major and minor additional constituents.
([2]) The proportion of silica fumes is limited to 10 %.
([3]) Limestone up to 0.50 % TOC
([4]) Limestone up to 0.20 % TOC
([5]) In Portland-composite cements CEM II/A-M and CEM II/B-M, in pozzolanic cements CEM IV/A and CEM IV/B and in composite cements CEM V/A and CEM V/B the main constituents other than clinker shall be declared by designation of the cement

*Source:* [149, CEN/EN 197-1, 2000]

Appendix 2: Granulometric analysis of the preliminary tests from #3 to #13.

| GRANULOMETRIC CURVE OF SAMPLE #3 | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 500 | 29,10 | 7,03 | 7,03 | 92,97 |
| 355 | 2,90 | 0,70 | 7,73 | 92,27 |
| 250 | 8,90 | 2,15 | 9,88 | 90,12 |
| 180 | 17,70 | 4,27 | 14,15 | 85,85 |
| 125 | 14,00 | 3,38 | 17,53 | 82,47 |
| 90 | 45,10 | 10,89 | 28,42 | 71,58 |
| 63 | 16,70 | 4,03 | 32,46 | 67,54 |
| 45 | 62,10 | 15,00 | 47,45 | 52,55 |
| Pan | 217,60 | 52,55 | 100,00 | 0,00 |
| Total | 414,10 | 100,00 | | |

| GRANULOMETRIC CURVE OF SAMPLE #4 | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 500 | 31,60 | 7,10 | 7,10 | 92,90 |
| 355 | 1,70 | 0,38 | 7,49 | 92,51 |
| 250 | 4,10 | 0,92 | 8,41 | 91,59 |
| 180 | 9,10 | 2,05 | 10,45 | 89,55 |
| 125 | 16,80 | 3,78 | 14,23 | 85,77 |
| 90 | 25,50 | 5,73 | 19,96 | 80,04 |
| 63 | 23,40 | 5,26 | 25,22 | 74,78 |
| 45 | 48,50 | 10,90 | 36,13 | 63,87 |
| Pan | 284,10 | 63,87 | 100,00 | 0,00 |
| Total | 444,80 | 100,00 | | |

| GRANULOMETRIC CURVE OF SAMPLE #5 | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 500 | 86,80 | 19,25 | 19,25 | 80,75 |
| 355 | 0,20 | 0,04 | 19,29 | 80,71 |
| 250 | 0,40 | 0,09 | 19,38 | 80,62 |
| 180 | 1,70 | 0,38 | 19,76 | 80,24 |
| 125 | 6,20 | 1,38 | 21,14 | 78,86 |
| 90 | 23,00 | 5,10 | 26,24 | 73,76 |
| 63 | 69,40 | 15,39 | 41,63 | 58,37 |
| 45 | 113,70 | 25,22 | 66,84 | 33,16 |
| 32 | 132,90 | 29,47 | 96,32 | 3,68 |
| Pan | 16,60 | 3,68 | 100,00 | 0,00 |
| Total | 450,90 | 100,00 | | |

| GRANULOMETRIC CURVE OF SAMPLE #6 | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 5600 | 0,00 | 0,00 | 0,00 | 100,00 |
| 4000 | 0,60 | 0,14 | 0,14 | 99,86 |
| 2800 | 0,80 | 0,19 | 0,33 | 99,67 |
| 2000 | 0,80 | 0,19 | 0,51 | 99,49 |
| 1400 | 1,20 | 0,28 | 0,79 | 99,21 |
| 1000 | 1,40 | 0,33 | 1,12 | 98,88 |
| 710 | 4,70 | 1,10 | 2,22 | 97,78 |
| 500 | 1,50 | 0,35 | 2,57 | 97,43 |
| 355 | 9,20 | 2,15 | 4,72 | 95,28 |
| 250 | 22,70 | 5,31 | 10,03 | 89,97 |
| 180 | 18,20 | 4,26 | 14,29 | 85,71 |
| 125 | 116,60 | 27,26 | 41,55 | 58,45 |
| 90 | 78,60 | 18,38 | 59,93 | 40,07 |
| 63 | 100,40 | 23,47 | 83,40 | 16,60 |
| 45 | 54,30 | 12,70 | 96,10 | 3,90 |
| 32 | 11,10 | 2,60 | 98,69 | 1,31 |
| Pan | 5,60 | 1,31 | 100,00 | 0,00 |
| Total | 427,70 | 100 | | |

| GRANULOMETRIC CURVE OF SAMPLE #7 | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 16000 | 0,00 | 0,00 | 0,00 | 100,00 |
| 11200 | 18,50 | 4,16 | 4,16 | 95,84 |
| 8000 | 3,50 | 0,79 | 4,95 | 95,05 |
| 5600 | 0,00 | 0,00 | 4,95 | 95,05 |
| 4000 | 0,10 | 0,02 | 4,97 | 95,03 |
| 2800 | 1,10 | 0,25 | 5,22 | 94,78 |
| 2000 | 0,80 | 0,18 | 5,40 | 94,60 |
| 1400 | 0,20 | 0,04 | 5,44 | 94,56 |
| 1000 | 0,10 | 0,02 | 5,46 | 94,54 |
| 710 | 0,40 | 0,09 | 5,55 | 94,45 |
| 500 | 0,30 | 0,07 | 5,62 | 94,38 |
| 355 | 1,20 | 0,27 | 5,89 | 94,11 |
| 250 | 5,10 | 1,15 | 7,04 | 92,96 |
| 180 | 10,60 | 2,38 | 9,42 | 90,58 |
| 125 | 26,90 | 6,05 | 15,47 | 84,53 |
| 90 | 18,10 | 4,07 | 19,54 | 80,46 |
| 63 | 17,50 | 3,94 | 23,48 | 76,52 |
| 45 | 33,40 | 7,51 | 30,99 | 69,01 |
| 32 | 80,20 | 18,03 | 49,02 | 50,98 |
| Pan | 226,70 | 50,98 | 100,00 | 0,00 |
| Total | 444,70 | 100,00 | | |

| GRANULOMETRIC CURVE OF SAMPLE #8 | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 22400 | 0 | 0,00 | 0,00 | 100,00 |
| 16000 | 7,7 | 1,67 | 1,67 | 98,33 |
| 11200 | 0 | 0,00 | 1,67 | 98,33 |
| 8000 | 0 | 0,00 | 1,67 | 98,33 |
| 5600 | 0 | 0,00 | 1,67 | 98,33 |
| 4000 | 0,05 | 0,01 | 1,68 | 98,32 |
| 2800 | 0,5 | 0,11 | 1,79 | 98,21 |
| 2000 | 0,4 | 0,09 | 1,88 | 98,12 |
| 1400 | 0,1 | 0,02 | 1,90 | 98,10 |
| 1000 | 0,1 | 0,02 | 1,92 | 98,08 |
| 710 | 0,9 | 0,20 | 2,12 | 97,88 |
| 500 | 0,6 | 0,13 | 2,25 | 97,75 |
| 355 | 1,2 | 0,26 | 2,51 | 97,49 |
| 250 | 4,2 | 0,91 | 3,42 | 96,58 |
| 180 | 7,6 | 1,65 | 5,07 | 94,93 |
| 125 | 18,8 | 4,08 | 9,15 | 90,85 |
| 90 | 14,6 | 3,17 | 12,32 | 87,68 |
| 63 | 19 | 4,12 | 16,44 | 83,56 |
| 45 | 41,6 | 9,03 | 25,47 | 74,53 |
| 32 | 162,6 | 35,29 | 60,76 | 39,24 |
| Pan | 180,8 | 39,24 | 100,00 | 0,00 |
| Total | 460,75 | 100,00 | | |

| GRANULOMETRIC CURVE OF SAMPLE #9 | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 5600 | 0,00 | 0,00 | 0,00 | 100,00 |
| 4000 | 0,05 | 0,01 | 0,01 | 99,99 |
| 2800 | 0,70 | 0,16 | 0,17 | 99,83 |
| 2000 | 0,30 | 0,07 | 0,23 | 99,77 |
| 1400 | 0,60 | 0,13 | 0,37 | 99,63 |
| 1000 | 0,90 | 0,20 | 0,57 | 99,43 |
| 710 | 2,80 | 0,63 | 1,20 | 98,80 |
| 500 | 0,05 | 0,01 | 1,21 | 98,79 |
| 355 | 0,60 | 0,13 | 1,34 | 98,66 |
| 250 | 4,70 | 1,05 | 2,39 | 97,61 |
| 180 | 9,10 | 2,04 | 4,43 | 95,57 |
| 125 | 16,70 | 3,74 | 8,17 | 91,83 |
| 90 | 10,80 | 2,42 | 10,58 | 89,42 |
| 63 | 23,70 | 5,30 | 15,89 | 84,11 |
| 45 | 28,40 | 6,35 | 22,24 | 77,76 |
| 32 | 87,20 | 19,51 | 41,75 | 58,25 |
| Pan | 260,30 | 58,25 | 100,00 | 0,00 |
| Total | 446,90 | 100,00 | | |

| GRANULOMETRIC CURVE OF SAMPLE #10a | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 2800 | | 0,00 | 0,00 | 100,00 |
| 2000 | 0,20 | 0,04 | 0,04 | 99,96 |
| 1400 | 0,30 | 0,07 | 0,11 | 99,89 |
| 1000 | 0,40 | 0,09 | 0,20 | 99,80 |
| 710 | 3,20 | 0,70 | 0,89 | 99,11 |
| 500 | 0,70 | 0,15 | 1,05 | 98,95 |
| 355 | 1,80 | 0,39 | 1,44 | 98,56 |
| 250 | 4,20 | 0,91 | 2,35 | 97,65 |
| 180 | 6,70 | 1,46 | 3,81 | 96,19 |
| 125 | 26,20 | 5,71 | 9,52 | 90,48 |
| 90 | 16,70 | 3,64 | 13,16 | 86,84 |
| 63 | 21,90 | 4,77 | 17,93 | 82,07 |
| 45 | 38,30 | 8,34 | 26,27 | 73,73 |
| 32 | 110,90 | 24,16 | 50,42 | 49,58 |
| Pan | 227,60 | 49,58 | 100,00 | 0,00 |
| Total | 459,10 | 100,00 | | |

| GRANULOMETRIC CURVE OF SAMPLE #10b | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 2000 | 0,00 | 0,00 | 0,00 | 100,00 |
| 1400 | 0,20 | 0,04 | 0,04 | 99,96 |
| 1000 | 0,10 | 0,02 | 0,07 | 99,93 |
| 710 | 0,30 | 0,07 | 0,13 | 99,87 |
| 500 | 1,20 | 0,27 | 0,40 | 99,60 |
| 355 | 2,50 | 0,56 | 0,96 | 99,04 |
| 250 | 7,30 | 1,63 | 2,60 | 97,40 |
| 180 | 9,00 | 2,01 | 4,61 | 95,39 |
| 125 | 44,90 | 10,05 | 14,66 | 85,34 |
| 90 | 7,90 | 1,77 | 16,42 | 83,58 |
| 63 | 16,10 | 3,60 | 20,03 | 79,97 |
| 45 | 33,50 | 7,50 | 27,52 | 72,48 |
| 32 | 114,50 | 25,62 | 53,14 | 46,86 |
| Pan | 209,40 | 46,86 | 100,00 | 0,00 |
| Total | 446,90 | 100,00 | | |

| GRANULOMETRIC CURVE OF SAMPLE #11 | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 4000 | 0,00 | 0,00 | 0,00 | 100,00 |
| 2800 | 0,30 | 0,07 | 0,07 | 99,93 |
| 2000 | 0,10 | 0,02 | 0,09 | 99,91 |
| 1400 | 0,10 | 0,02 | 0,11 | 99,89 |
| 1000 | 0,20 | 0,04 | 0,15 | 99,85 |
| 710 | 0,80 | 0,18 | 0,33 | 99,67 |
| 500 | 1,80 | 0,40 | 0,73 | 99,27 |
| 355 | 2,40 | 0,53 | 1,25 | 98,75 |
| 250 | 4,50 | 0,99 | 2,24 | 97,76 |
| 180 | 6,80 | 1,50 | 3,74 | 96,26 |
| 125 | 19,40 | 4,27 | 8,01 | 91,99 |
| 90 | 13,30 | 2,93 | 10,93 | 89,07 |
| 63 | 20,30 | 4,46 | 15,39 | 84,61 |
| 45 | 43,80 | 9,63 | 25,03 | 74,97 |
| 32 | 139,60 | 30,70 | 55,73 | 44,27 |
| Pan | 201,30 | 44,27 | 100,00 | 0,00 |
| Total | 454,70 | 100,00 | | |

| GRANULOMETRIC CURVE OF SAMPLE #12a | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 11200 | 0,00 | 0,00 | 0,00 | 100,00 |
| 8000 | 2,10 | 0,47 | 0,47 | 99,53 |
| 5600 | 0,00 | 0,00 | 0,47 | 99,53 |
| 4000 | 0,00 | 0,00 | 0,47 | 99,53 |
| 2800 | 0,40 | 0,09 | 0,56 | 99,44 |
| 2000 | 0,50 | 0,11 | 0,67 | 99,33 |
| 1400 | 0,20 | 0,04 | 0,71 | 99,29 |
| 1000 | 0,30 | 0,07 | 0,78 | 99,22 |
| 710 | 0,90 | 0,20 | 0,98 | 99,02 |
| 500 | 1,90 | 0,42 | 1,41 | 98,59 |
| 355 | 1,80 | 0,40 | 1,81 | 98,19 |
| 250 | 3,80 | 0,85 | 2,66 | 97,34 |
| 180 | 6,60 | 1,47 | 4,13 | 95,87 |
| 125 | 19,10 | 4,26 | 8,39 | 91,61 |
| 90 | 8,40 | 1,87 | 10,26 | 89,74 |
| 63 | 19,40 | 4,33 | 14,59 | 85,41 |
| 45 | 40,80 | 9,10 | 23,69 | 76,31 |
| 32 | 193,80 | 43,24 | 66,93 | 33,07 |
| Pan | 148,20 | 33,07 | 100,00 | 0,00 |
| Total | 448,20 | 100,00 | | |

| GRANULOMETRIC CURVE OF SAMPLE #12b | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 8000 | 0,00 | 0,00 | 0,00 | 100,00 |
| 5600 | 0,90 | 0,22 | 0,22 | 99,78 |
| 4000 | 0,00 | 0,00 | 0,22 | 99,78 |
| 2800 | 0,20 | 0,05 | 0,26 | 99,74 |
| 2000 | 0,05 | 0,01 | 0,28 | 99,72 |
| 1400 | 0,05 | 0,01 | 0,29 | 99,71 |
| 1000 | 0,05 | 0,01 | 0,30 | 99,70 |
| 710 | 0,40 | 0,10 | 0,40 | 99,60 |
| 500 | 1,00 | 0,24 | 0,64 | 99,36 |
| 355 | 3,90 | 0,94 | 1,57 | 98,43 |
| 250 | 3,70 | 0,89 | 2,46 | 97,54 |
| 180 | 4,90 | 1,18 | 3,64 | 96,36 |
| 125 | 24,00 | 5,77 | 9,41 | 90,59 |
| 90 | 9,60 | 2,31 | 11,72 | 88,28 |
| 63 | 20,00 | 4,81 | 16,53 | 83,47 |
| 45 | 33,60 | 8,08 | 24,61 | 75,39 |
| 32 | 201,00 | 48,32 | 72,93 | 27,07 |
| Pan | 112,60 | 27,07 | 100,00 | 0,00 |
| Total | 415,95 | 100,00 | | |

| GRANULOMETRIC CURVE OF SAMPLE #13 | | | | |
|---|---|---|---|---|
| **Sieve opening (µm)** | **Weight retained (g)** | **Percentage retained (%)** | **Accumulated retained percentage (%)** | **Passing percentage (%)** |
| 2800 | 0,00 | 0,00 | 0,00 | 100,00 |
| 2000 | 0,40 | 0,09 | 0,09 | 99,91 |
| 1400 | 0,00 | 0,00 | 0,09 | 99,91 |
| 1000 | 0,00 | 0,00 | 0,09 | 99,91 |
| 710 | 0,40 | 0,09 | 0,18 | 99,82 |
| 500 | 0,80 | 0,18 | 0,35 | 99,65 |
| 355 | 1,40 | 0,31 | 0,66 | 99,34 |
| 250 | 3,40 | 0,75 | 1,42 | 98,58 |
| 180 | 5,70 | 1,26 | 2,68 | 97,32 |
| 125 | 16,90 | 3,74 | 6,42 | 93,58 |
| 90 | 9,50 | 2,10 | 8,52 | 91,48 |
| 63 | 36,10 | 7,99 | 16,52 | 83,48 |
| 45 | 29,10 | 6,44 | 22,96 | 77,04 |
| 32 | 198,80 | 44,01 | 66,97 | 33,03 |
| Pan | 149,20 | 33,03 | 100,00 | 0,00 |
| Total | 451,70 | 100,00 | | |