

**STUDY OF CLINKER GRINDABILITY FROM  
YTL CEMENT, KANTHAN, PERAK**

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**STUDY OF CLINKER GRINDABILITY FROM YTL CEMENT,  
KANTHAN, PERAK**

by

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## DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Study of Clinker Grindability From YTL Cement, Kanthan, Perak”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this of any other examining body or University.

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## LIST OF SYMBOLS

$\text{Ca}_3\text{Al}_2\text{O}_6$	Tricalcium Aluminate
$3\text{CaO}\cdot\text{SiO}_2$	Calcium Silicates
$\text{C}_3\text{S}$	Alite
$\text{C}_2\text{S}$	Belite
$\text{C}_3\text{A}$	Aluminate
$\text{C}_4\text{AF}$	Ferrite
$\text{Ca}_3\text{SiO}_5$	Tricalcium Silicate
$\text{Ca}_2\text{SiO}_4$	Dicalcium Silicate
$\text{Ca}_4\text{AlFeO}_5$	Tetracalcium Aluminoferrite
$\text{HF}$	Hydrofluoric
$\text{CaMg}(\text{CO}_3)_2$	Dolomite
$\text{P}_2\text{O}_5$	Phosphorus pentoxide

## **LIST OF ABBREVIATIONS**

USM	Universiti Sains Malaysia
OPC	Ordinary Portland Cement

## **LIST OF APPENDICES**

Appendix A      Data Collections for Grindability Approved Clinker

Appendix B      Data Collections for Grindability Outspec Clinker

## ABSTRAK

Kualiti bahan mentah, perubahan kimia yang berlaku sepanjang proses pembakaran dan penyejukan, dan tahap pengisaran semuanya mempengaruhi kualiti produk akhir klinker. Kajian tentang mineralogi dan kimia klinker akan mendedahkan butiran tentang sifat bahan dan keadaan yang berlaku semasa peringkat pembuatan yang berbeza. Penyelidikan dilakukan ke atas faktor-faktor yang mempengaruhi kebolehkisaran semasa klinking, termasuk fasa primer (alit, belit, aluminat, dan ferit), tahap penghabluran, saiz kristal alit, dan kelompok belit. Sejumlah tinggi alit dan kandungan rendah fasa belit dan interstisial (aluminat dan ferit) lebih mudah dikisar berbanding klinker yang kaya dengan fasa belit dan interstisial. Dapati bahawa pengisaran klinker bergantung kepada komposisi kimia dan ciri mineralogi. Kebolehkisaran dipengaruhi lagi oleh gugusan belite dan saiz gugusan kristal. Kebolehkisaran klinker diperkukuh lagi dengan menjalankan ujian indeks kebolehkisaran yang mana ujian indeks kebolehkisaran mengukur sejauh mana bahan akan tahan untuk dikisar dalam kilang bebola. Indeks Kebolehkisaran pelbagai bijih boleh dikira dan dibandingkan menggunakan ujian ini. Semakin sukar untuk mengisar bahan, semakin tinggi indeks kebolehkisaran.

**STUDY OF CLINKER GRINDABILITY FROM YTL CEMENT, KANTHAN,  
PERAK**

**ABSTRACT**

The quality of the raw material, the chemical changes that occur throughout the burning and cooling processes, and the degree of grinding all affect the final clinker product's quality. Studies on clinker's mineralogy and chemistry will reveal details on the material's properties and the circumstances that prevail during different manufacturing stages. Research done into the factors that affect grindability during clinkering, including the primary phase (alite, belite, aluminate, and ferrite), degree of crystallisation, alite crystal size, and belite clusters. A high amount of alite and low content of belite and interstitial phases (aluminate and ferrite) are easier to grind rather than the clinker rich with belite and interstitial phases. Discover that the grinding of clinker depends on the chemical composition and mineralogical features. Grindability is further impacted by belite clusters and alite crystal cluster size. The grindability of the clinker reinforced again by running grindability index test which a grindability index test measures how well a material will hold up to being ground in a ball mill. The Grindability Index of various ores may be calculated and compared using this test. The harder it is to grind the material, the higher the grindability index.

# CHAPTER 1

## INTRODUCTION

### 1.1 Background Project

In this project, the clinker sample was collected at YTL Cement, Kanthan, Perak. Two main types of clinker was selected which are approved clinker and the other one is outspec clinker. Approved clinker means the company select as product while outspec clinker is rejected clinker due to some reasons. This project will find out the possible reasons that may lead to the rejection. The basic materials for cement manufacturing include a mixture of minerals containing calcium oxide, silicon oxide, aluminium oxide, ferric oxide, and magnesium oxide (as fine powder). The raw ingredients are typically extracted from local rocks, which in some cases are practically the desired composition, while in others, clay and limestone, as well as iron ore, bauxite, or recycled materials, are required. The chemical composition of feed has a significant impact on fuel consumption, kiln operation, clinker production, and cement performance. Further discussion will be continue regarding to the physical characteristic of the clinker comparison by naked eye and optical microscopic examination.

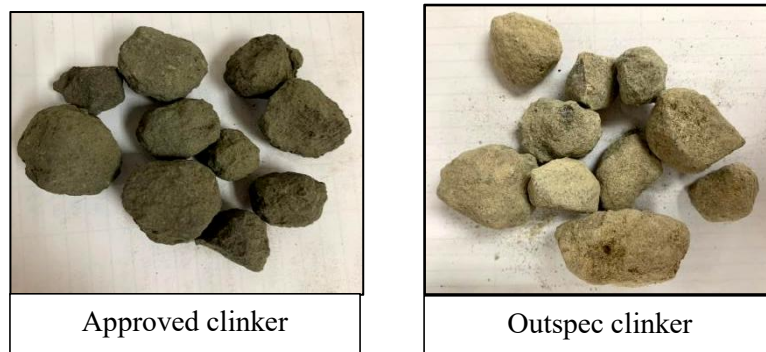


Figure 1.1 : Different between approved clinker and outspec clinker



## **1.2 Problem Statement**

Since clinker grinding consumes a significant amount of energy in a cement plant, improving clinker grindability would boost grinding efficiency and lowering energy consumption. The ease with which clinker may be ground is determined by a variety of factors, including porosity, content, and crystal size. Clinker grinding consumes around 2.5 kWh/tonne of clinker produced. Cement manufacture is expensive due to these and other pyroprocessing characteristics. As a result, the pyroprocessing process in kilns, as well as the grinding technologies must be tuned for optimal processing.

## **1.3 Objectives**

The objectives of this study include :-

1. To investigate the effects of clinker microstructure on the quality cement production.
2. To determine the standard work index for reduce the material size.

## **1.4 Scope of Research**

The study of clinker grindability involving several assessments such as particle size distribution, clinker microscopy examination, and bond grindability test.

Chapter 2 will cover the clinker formation and raw material of clinker production which then indicates the chemical composition found in clinker. This section will demonstrate the previous studies regarding microscopic characterization of clinker phase which known as alite, belite aluminate and ferrite.

Chapter 3 will explain in details the procedure of the analysis performed in the characterization of clinker sample. Half of the samples have undergone

microscopy examination to further analyzed for elemental composition and identification of clinker phases. Whereas, another half of the samples will be used for particle size distribution and bond grindability test.

The results from overall analysis performed will be discussed in Chapter 4. The outcome from elemental composition and clinker phase identification are verified by the results from optical microscopy examination. Meanwhile, other than identification of size ranges from particle size distribution, the grinding quality and work index of the grindability also can be obtained from the bond grindability test.

Lastly, the conclusion from the results obtained will be wrap up in Chapter 5 in agreement with the objectives of this grindability studies. Moreover, the recommendation for future studies are added in this chapter to improvise the experimental work for a best result.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Introduction

Clinker is a nodular material created during the kilning step of cement manufacture and is utilised as a binder in a variety of cement products. Clinker lumps or nodules are usually 3-25 mm in diameter and dark grey in appearance. In a rotating kiln, limestone and clay are heated to the point of liquefaction at around 1400°C-1500°C. Pyroprocessing is a crucial step in the cement making process. Materials are heated to high temperatures produce a chemical or physical change in this process. Its control optimises energy usage efficiency and, as a result, increases output for high quality assurance (Nalobile et al.). The nature of kilns used in cement manufacture is complex. They have longer time constants and unprocessed data. The materials utilised have a wide range of qualities (Saidur et al.). As a result, they're challenging to manage. In addition, the inclusion of a variety of alternate options because the fuel qualities remain uneven throughout the kiln operation, using different fuels complicates the process. The fuel intensity regulations for kilns that use fuel oil are extremely high, ranging from 2.9 to 7.5 GJ/ton of clinker produced (Nalobile et al.). Then, clinker is pulverised finely and mixed with gypsum (to control the setting qualities of cement and assure compressive strength). Clinker may be stored in a dry state for long periods of time without losing quality, which is why it is traded internationally and used by cement manufacturers when raw materials are rare or unavailable. Clinker grinding consumes around 2.5 kWh/tonne of clinker produced. Cement manufacture is expensive due to these and other pyroprocessing characteristics. As a result, the pyroprocessing process in kilns, as well as the grinding technologies must be tuned for optimal processing.

## 2.2 Types of Clinker

There are five different special types of cement clinker which as follows :-

Table 2.1 : The different types of clinker

Types of clinker	Descriptions
Surface Resistant Clinker	It contains 76% alite, 5% belite, 2% tricalcium aluminate, 16% tetracalcium aluminoferrite, and 1% free calcium oxide. Its production has decreased in recent years as sulfate resistance can be easily achieved by using granulated blast furnace slag in cement production.
Low Heat Clinker	With relatively little free lime, it comprises 29% alite, 54% belite, 2% tricalcium aluminate, and 15% tetracalcium aluminoferrite. It is no longer manufactured since cement made from regular clinker and pulverised granulated blast furnace slag has good low heat characteristics.
White Clinker	It is 76% alite, 15% belite, 7% tricalcium aluminate, 2% free lime, and no tetracalcium aluminoferrite. The composition, on the other hand, might vary greatly. It manufactures white cement, which is utilised in building for aesthetic purposes. The vast majority of it is used in factory-made pre-cast concrete applications.
Low Alkali Clinker	Clinker's alkali concentration is lowered by substituting the raw-mix alumina source with another component or by installing a "alkali bleed." It entailed removing part of the kiln system's high temperature gases, which resulted in considerable heat loss.
Belite Calciumsulfoaluminate Ternesite (BCT)	This technique is employed in the production of clinker that emits up to 30% less CO <sub>2</sub> . It helps to increase energy efficiency. In addition, the manufacturing process's power costs are around 15% lower.

### 2.3 Raw Material

The raw material cement composition varies from plant to plant due to cement standards as well as mineralogy of available resources. In general, however, a eutectic mix is sought that minimises the amount of heat required for clinkering as well as the total cost of raw materials while generating a satisfactory cement. The raw materials used are generally 80% limestone, 15-20% clay or shale, and 2-5% sand or iron ore, and Ordinary Portland cement is made up of four major chemicals which are carbonates, aluminosilicates, iron and aluminium compounds (oxides), and minor constituents. The first three compounds are very important in the production of cement clinker, whilst the fourth will have an impact on the manufacturing process, namely burning, kiln stabilisation, and pre-heating performance, depending on the kind and quantity of minor elements present (Musa,2002).

The chemical homogeneity of the feed has a significant impact on cement performance, kiln operation, fuel consumption, and clinker formation (Ibrahim, 2010).

Table 2.2 shows typical raw mix on clinker, its an approximate analysis is :

Table 2.2 : Typical chemical analysis of kiln feed raw material (Alsop et al, 2007)

CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	Mn <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O
65-68%	20-23%	4-6%	2-4%	1-5%	0.1-3%	0.1-1%	0.1 - 2%	0.1-1%	0.1-0.5%

Variations in the kiln feed chemical composition affect its burnability and eventually the fuel consumption. For a long time, cement was produced using practical expertise gained throughout the manufacturing process. When chemical studies of Portland cement (feed raw materials and clinker) were compared, it was discovered that certain relationships exist between the proportion of lime on the one

hand and the combination of silica, alumina, and iron oxide on the other. These modulus are :-

### 2.3.1 Hydraulic Modulus (HM)

The hydraulic modulus is generally limited by the values (1.7-2.3), which has the following form :

$$HM = \frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3}$$

It was discovered that when HM increases, more heat is required for clinker burning; the strengths, particularly the first strengths set up, and the heat of hydration grow; and the resistance to chemical attack declines. Cements with HM less than 1.7 exhibited mainly inadequate strength, whereas cements with HM larger than 2.3 exhibited poor volume stability.

### 2.3.2 Silica Ratio (SR)

It is the proportion of SiO<sub>2</sub> to the total of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, given as following :

$$SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3}$$

Increasing the silica ratio reduces clinker burnability through lowering liquid phase concentration and the potential for coating development in the kiln. The cement hardens and sets slowly as the silica percentage increases. The amount of liquid phase increases as the silica ratio decreases, improving clinker burnability and coating development in the kiln. In general, the silica ratio ranges between (1.9-3.2), however low values for silica ratios can be tolerated as low as 1.5.

### 2.3.3 Alumina Ratio (AR)

It is characterizing the cement by the proportion of alumina to iron oxide, given as following :

$$AR = \frac{Al_2O_3}{Fe_2O_3}$$

Alumina ratio values vary between 1.5 and 2.5. When the AR is less than 1.5, both oxides are present in their molecular ratios and so only tetracalcium aluminoferrite may be generated in the clinker; as a result, the clinker cannot include tricalcium aluminate. This is the case with Ferrari-cement, which has a low heat of hydration, slow setting, and low shrinkage. A high alumina ratio combined with a low silica ratio leads in a quick setting cement, which necessitates the inclusion of a greater gypsum rate to limit the setting time.

### 2.3.4 Lime Saturation Factor (LSF)

To attain complete lime saturation in the clinker the total silica must be combined as C<sub>3</sub>S, all iron oxide must combine with the equivalent amount of alumina to C<sub>4</sub>AF, and the remaining alumina must combine to C<sub>3</sub>A. This formula expressed as following for MgO lower than 2%.

$$LSF = \frac{100 (CaO + 0.75 MgO)}{2.85 SiO_2 + 1.18 Al_2O_3 + 0.65 Fe_2O_3}$$

For technical purposes good values ranged between (80-95).

Table 2.2 below show the chemical composition of raw materials that used in Al-Mergheb cement plant (one of Alahlia cement company, Khoms city, Libya) where they find it very normal for operation, so require proportions of mix may be obtained easily then fed to kiln to form a clinker.

Table 2.3 : Chemical composition of raw materials used to preparing kiln feed mix

(Ibrahim, 2010)

<b>Composition</b>	<b>Limestone</b>	<b>Marl</b>	<b>Iron Ore</b>	<b>Clay</b>
<b>SiO<sub>2</sub></b>	8.34	27.98	8.56	53.75
<b>Al<sub>2</sub>O<sub>3</sub></b>	2.74	10.87	6.79	14.4
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0.94	3.08	68.69	4.99
<b>CaO</b>	47.62	30.12	5.97	8.71
<b>MgO</b>	0.97	1.95	0.481	1.8
<b>SO<sub>3</sub></b>	0	0.7	0.901	0.31
<b>K<sub>2</sub>O</b>	0.39	0.2	0.151	1.99
<b>Na<sub>2</sub>O</b>	0.04	0.33	0.177	0.62
<b>LOI</b>	38.54	24.68	5	13.37
<b>Rest</b>	0.42	0.09	3.28	0.06
<b>Total</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>

The lime component in cement raw materials is typically represented at 76-80%. As a result, the chemical and physical qualities of this component have a significant impact on the process of cement manufacturing as well as the kind of production machine used (Vuk et al, 2020). Limestone is a common calcareous component that is also an essential element in the manufacture of cement and a raw material in the creation of clinker. It has a mostly fine-grained crystalline structure with a hardness range of 1.8 to 3.0 on the Mohr's hardness scale. Although the purest limestone is white in colour, it may include magnesium, aluminium, and iron in the form of carbonates and silicates. Some limestone contains dolomite  $\text{CaMg}(\text{CO}_3)_2$ , which introduces magnesium oxide into the basic material



A reasonable proportion of magnesium oxide, not to exceed 4%, can reduce the clinkering temperature, enhance tricalcium silicate formation, and aid in the coexistence of the two minerals in the clinker. Phosphorus pentoxide  $P_2O_5$ , of more than 0.3% can lead to a problem because it stabilizes belite and inhibits alite formation in the kiln and may also extend setting times for the finished cement (Altun, 1999). Clay is another major ingredient used in cement production, accounting for roughly 15-20% of the raw mix component. Clay used in cement production is often a blend of kaolinite and illitic minerals. Clays are typically hydrous alumino-silicates with a wide range of compositions. This fluctuation is determined by the clay minerals present and their quantity, and these clay minerals have an influence on cement production (Musa, 2002). They also have a significant impact on the pelletizing or nodulizing qualities of the raw mix, as well as the water demand of the raw slurry in the wet cement manufacturing process. Moreover, low quality clays associated with high content of free silica (as quartz) also lead to an emerging problem in cement process. The percentage of free quartz in clay should be kept below 65% since it can impair both the grindability and the burnability of the raw mix. Other than that, an increase in the amount of  $Fe_2O_3$  can decrease the amount of alite ( $C_3S$ ) resulting the formation of more belite ( $C_2S$ ) which is lead to poor grindability and produce low physio-mechanical strength.

Chemical compositions of kiln feed that product as result of mixing processes also for the clinker formed throughout the kiln are shown in Table 2.3 in which the kiln operating at ideal case (normal operating state). While Table 2.4 shows the chemical composition of kiln feed mix (field data of non-ideal operation).

Table 2.4 Chemical composition of kiln feed mix and clinker formed  
(field data of ideal operation) (Ibrahim,2010)

<b>Component</b>	<b>Kiln Feed</b>	<b>Clinker Formed</b>
<b>SiO<sub>2</sub></b>	14.43	22.22
<b>Al<sub>2</sub>O<sub>3</sub></b>	3.9	5.87
<b>Fe<sub>2</sub>O<sub>3</sub></b>	2.27	3.45
<b>CaO</b>	42.61	65.13
<b>MgO</b>	1.09	1.65
<b>SO<sub>3</sub></b>	0.1	0.15
<b>K<sub>2</sub>O</b>	0.9	1.37
<b>Na<sub>2</sub>O</b>	0.09	0.13
<b>LOI</b>	34.61	-
<b>Total</b>	100	100
<b>CaCO<sub>3</sub> content</b>	76.09	-

Table 2.5 Chemical composition of kiln feed mix (field data of non-ideal operation)  
(Ibrahim, 2010)

<b>Component</b>	<b>Kiln Feed Case 1</b>	<b>Kiln Feed Case 2</b>	<b>Kiln Feed Case 3</b>
<b>SiO<sub>2</sub></b>	11.60	11.61	11.61
<b>Al<sub>2</sub>O<sub>3</sub></b>	2.52	2.51	2.52
<b>Fe<sub>2</sub>O<sub>3</sub></b>	2.05	2.05	2.05
<b>CaO</b>	44.24	44.26	44.26
<b>MgO</b>	1.42	1.41	1.40
<b>SO<sub>3</sub></b>	0.217	0.22	0.21
<b>K<sub>2</sub>O</b>	0.78	0.70	0.78
<b>Na<sub>2</sub>O</b>	0.04	0.08	0.04
<b>LOI</b>	37.27	37.28	37.28
<b>Total</b>	100.16	100.25	100.29
<b>CaCO<sub>3</sub> content</b>	79	79.05	70.05

Table 2.4 describe the chemical composition of the final result of the mixing process that is given to the kiln (kiln feed) for the same raw materials reported in Table 2.2. This combination is hard burning without clinker formation in which the kiln operation is non-ideal. Many issues arise as a result of the process of hard burning (as discussed previously). According to Table 2.4, the chemical composition of this kiln feed mixture is not homogeneous as required in terms of the amount of calcium carbonate content is higher than that required for optimum operating (it is 79-79.05%), whereas for optimum operating the chemical composition of kiln feed must be ranged (76-76.5%), resulting in soft burning of kiln feed and clinker formation. Also, amount of fuel used for burning will be in economic range.

Alkalis and sulphate become more unstable when the kiln is operated on the hot side. As a result, build-ups in the colder areas of the kiln system may become more likely. Controlling the kiln may become challenging in severe circumstances due to material surges through the kiln. Hard burning causes low clinker porosity, big alite crystals, and frequently contributes to the creation of dust rather than excellent, nodular clinker. It also slows down the cooling process, due to the greater maximum temperature and the difficulty of cooling low-porosity clinker.

### 2.3.5 Bogue Formula

These formulae are the most essential and often used indications of a cement's or clinker's chemical qualities for a cement scientist. However, the elements determined by these methods are simply the potential compositions once the clinker has been burnt and cooled under certain conditions. Changes in cooling pace or burning temperature can significantly alter the real component makeup. When a significant quantity of SO<sub>3</sub> and Mn<sub>2</sub>O<sub>3</sub> are present in the clinker, the chemical analysis values must be adjusted to account for the amount of CaO mixed with SO<sub>3</sub>, the amount of free lime present, and the Mn<sub>2</sub>O<sub>3</sub>. The values to be used in the Bogue formulas are :-

$$\text{Fe}_2\text{O}_3 = \text{Fe}_2\text{O}_3 + \text{Mn}_2\text{O}_3$$

$$\text{CaO} = \text{CaO} - \text{free CaO} - (\text{CaO combined with SO}_3)$$

To find the amount of CaO that is combined with SO<sub>3</sub> as CaSO<sub>4</sub> proceed as follows :-

Step 1 : If  $(\text{K}_2\text{O}/\text{SO}_3) = < 1.176$  then not all of the SO<sub>3</sub> is combined with K<sub>2</sub>O as K<sub>2</sub>SO<sub>4</sub>.

$$\text{SO}_3 \text{ in K}_2\text{O} = 0.85 \text{ K}_2\text{O}$$

Step 2 : Calculate SO<sub>3</sub> residue

$$\text{SO}_3 - \text{SO}_3 (\text{in K}_2\text{O}) = \text{SO}_3 (\text{remaining})$$

If  $[\text{Na}_2\text{O}/\text{SO}_3 (\text{remain.})] = < 0.774$  then not all of the remaining SO<sub>3</sub> is combined with Na<sub>2</sub>O as Na<sub>2</sub>SO<sub>4</sub>.

$$\text{SO}_3 \text{ in Na}_2\text{O} = 1.292 \text{ Na}_2\text{O}$$

Step 3 : Calculate the amount of CaO that has combined with the SO<sub>3</sub> as CaSO<sub>4</sub>.

$$\text{CaO (in SO}_3) = 0.7 [ \text{SO}_3 - \text{SO}_3 (\text{in K}_2\text{O}) - \text{SO}_3 (\text{in Na}_2\text{O}) ]$$

After determining the proper CaO and Fe<sub>2</sub>O<sub>3</sub> levels, the probable clinker elements may be calculated using the previously provided Bogue formulae. When using the Bogue formulae for kiln feed compositions, take in mind that coal ash addition, dust losses, and alkali cycles can all change the ultimate clinker composition. In addition, the analysis must be performed on a "loss-free" basis in the constituent computations. Using examples above and the appropriate Bogue formulas, the following potential clinker compound content would be obtained :-

Table 2.6 Potential clinker compound content obtained from Bogue formula  
(Alsop et al, 2007)

<b>Compound</b>	<b>C<sub>3</sub>S</b>	<b>C<sub>2</sub>S</b>	<b>C<sub>3</sub>A</b>	<b>C<sub>4</sub>AF</b>
<b>Value from Bogue formula</b>	61.8	15.0	8.73	10.04

It should be emphasised once again that the clinker compounds computed by the Bogue formulae are just prospective in nature. These are formed depending on the temperature, period of exposure, and cooling rate of the clinker in the burning zone, and are considerably different from the estimated values.

## 2.4 Clinker Formation

Portland cement, also known as OPC or Ordinary Portland Cement, is the most widely used form of cement worldwide. CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> make up the majority of Portland cement clinker, accounting for more than 95% of the total. MgO, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, and alkalis are minor components that make up less than 3% of the total. Clinker is a semi-finished "cement" material by burning alumina, limestone, and clay (Al-Naffakh and Jafar, 2020). They do not exist as separate oxides in clinker, but rather as compounds created by two or more oxides. The mineral phases are exceedingly fine, ranging from 30 to 60µm. The clinker from Portland Cement is ground into a fine powder. Portland cement clinker is a hydraulic substance that must have at least two-thirds by mass of calcium silicates (3CaO.SiO<sub>2</sub> and 2CaO.SiO<sub>2</sub>), with the remaining portion made up of various compounds and phases of the clinker that contain iron and aluminium (Ibrahim, 2010).



Figure 2.1 : Physical difference between clinker and cement

There are two primary methods of producing cement which are the wet and dry production procedures. The main difference between the wet and dry processes is how the raw mix is prepared before the clinker is burned in the kiln. The wet method

involves adding water to the raw ingredients to create a thick raw slurry. Fine grinding and drying are used to prepare the raw materials in the dry process (Nalobile et al,2020). The process chosen is largely determined by the type of the raw materials available. When raw materials include more than 20% moisture, the wet process is recommended over the dry approach. Dry kilns now dominate the modern cement industry. Raw meal grinding, blending, pre-calcining, clinker burning, and cement grinding are all steps in the cement production process. All of these impacts might lead to cement with lower strength potential and higher water requirement. Reduced clinker porosity can make clinker more difficult to grind, increasing finish mill power usage or lowering mill output. Clinker temperatures may rise as they depart the cooler, increasing fuel consumption and posing handling issues. High-temperature circumstances may cause colour changes, decreases in clinker alkali and sulphate levels, and increases in water requirement due to increasing Aluminate levels.

Figure 2.2 below depicts the reactions that occur in a rotary kiln system. On the left is the feedstock, which in this case consists of calcite ( $\text{CaCO}_3$ ), quartz ( $\text{SiO}_2$ ), clay minerals ( $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ ), and iron oxide ( $\text{Fe}_2\text{O}_3$ ). Activation occurs by the elimination of water and changes in crystal structure up to a temperature of roughly  $700^\circ\text{C}$ . Decarbonation of calcium carbonate happens at temperatures ranging from  $700$  to  $900^\circ\text{C}$ , as does the first interaction of alumina, ferric oxide, and activated silica with lime. Belite develops at temperatures ranging from  $900$  to  $1200^\circ\text{C}$ . Above  $1250^\circ\text{C}$ , and especially above  $1300^\circ\text{C}$ , the liquid phase develops, promoting the interaction of belite with free lime to produce alite.

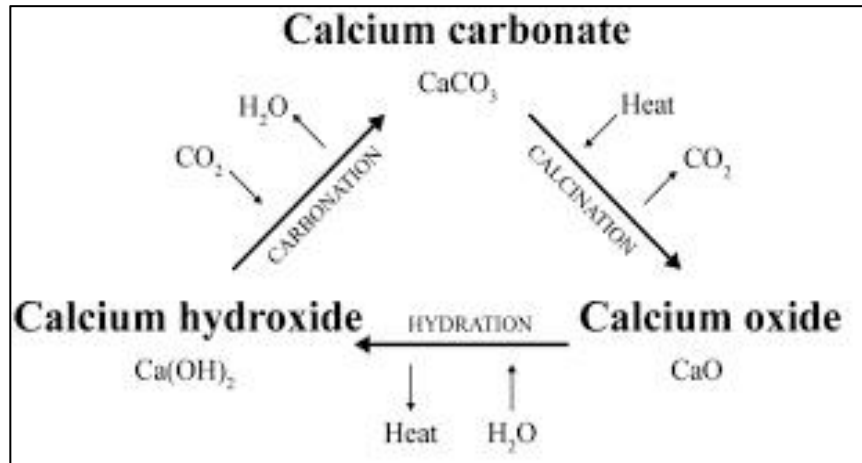


Figure 2.2 : The cycle of clinker formation process

The molten phase cools to a glass during the cooling stage on the right-hand side of the picture, or if cooling is sluggish, the C<sub>3</sub>A crystallises out, and in extreme situations, the Alite dissolves back into the liquid phase and reappears as secondary belite.

Chemical reactions may occur throughout the kiln:-

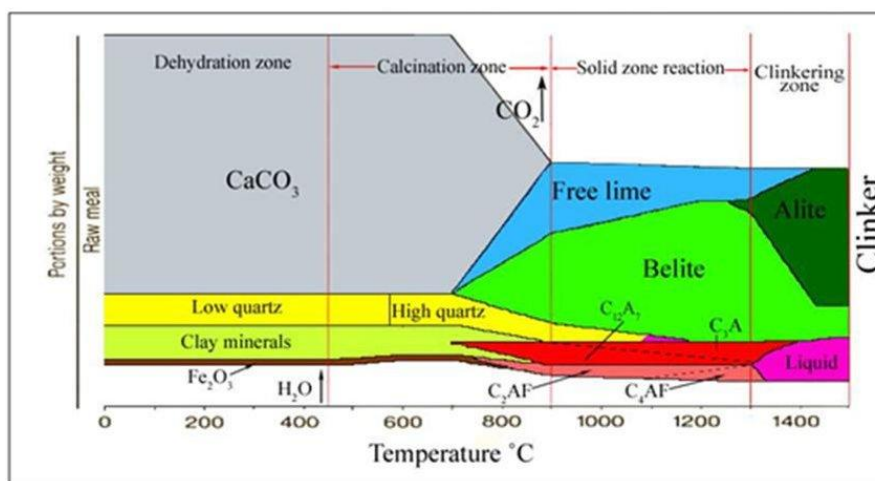
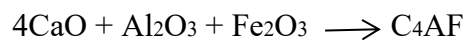
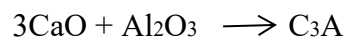
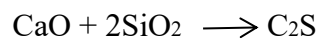
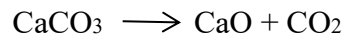


Figure 2.3 : A schematic view of the clinker formation reactions



## 2.5 Pyroprocessing

Cement manufacture in the world today which run pyroprocessing system that includes pre-heat, calcining, sintering (clinkering) and cooling. Calcining and clinkering were usually done in a rotary kiln. The raw ingredients are brought into the kiln at room temperature. The temperature within the kiln continues to climb, and when it reaches its peak, fast cooling produces clinker. Although the response phases frequently overlap, they may be described in a clear order as follows, free water evaporates at 65-125°C, thus latent heat must be provided. Net heat input per kilogramme of clinker is 2145 kJ. At 400-650°C endothermic decomposition of clays, and alkalis react with the kiln environment to generate liquid sulphates. There is 42.2 kJ/kg clinker net heat input. Dolomite decomposes endothermically around 500-650°C and 19.7 kJ of net energy input. Calcium carbonate combines endothermically with silica to generate "incipient belite" at temperatures ranging from 650 to 900°C and 722.5 kJ of net heat input. Calcium carbonate combines endothermically with alumina and iron oxide at 700-900°C to create aluminates and ferrite. The net heat input is 207.2 kJ. When all of the available silica, alumina, and iron oxide have been reacted, the remaining calcium carbonate decomposes endothermically to calcium oxide. The required heat input is 601.9 kJ/kg clinker. Aluminates, ferrite, and a portion of belite melt endothermically at 1300-1425°C, and belite reacts with calcium oxide to generate alite. At 1425-1300°C the melt re-freezes exothermically to aluminates, ferrite, and belite after passing peak temperature.

The basic mix is transformed into clinkers, which are grey, glass-hard, spherically shaped nodules with diameters ranging from 0.32 to 5.1 cm. Limestone and other calcium, silicon, aluminium, and iron oxide containing minerals are crushed and processed into a raw meal. The calcium carbonate is then heated in the pre-heating

system (cyclones) to begin the dissociation process of calcium carbonate to oxide. The meal is then heated in the kiln, where it undergoes a reaction between calcium oxide and carbon dioxide. At temperatures up to 1450 °C, additional elements combine to generate calcium silicates and aluminates, this is known as clinker burning. A riser duct connects the cyclone system to the rotary kiln. The riser duct is supplied secondary fuel, while the main fuel mixture, usually coal is utilised to light the fire. The reaction products leave the kiln as clinker, a nodular substance. If the pyroprocessing time is too short or the temperature is too low, the raw material component combination may be incomplete, resulting in some free unreacted lime. Inadequate raw mixture and blending management will result in substantial fluctuations in the chemical composition of the kiln feed. If the kiln is run at a consistent material residence time and temperature, the clinker composition, including free lime, will vary. This is significant because free lime is commonly used as a process measure to evaluate how efficiently the clinker burns. When unanticipated variations in kiln feed composition generate considerable variations in free lime, operators may make inaccurate kiln operation modifications, believing changes are required when they are not.

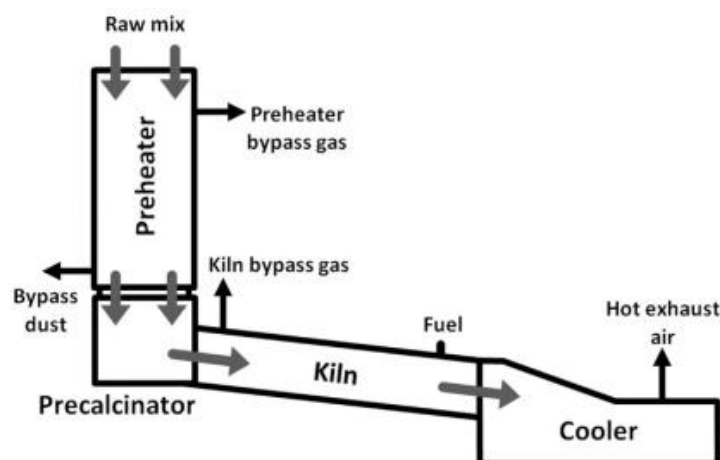


Figure 2.4 : Pyroprocessing processes in a dry kiln cement production plant

### **2.5.1 Pre-heat**

Preheaters are used in dry kiln cement plants to heat the raw mix and remove CO<sub>2</sub> and water before it is delivered into the kiln. The material in the kiln has a retention period of 30 to 40 minutes, the majority of which is in the burning zone. The temperature of the material rapidly rises from 850°C to 1250°C to 1300°C, at which point clinker melt forms. The chemical and physical changes of the material occur concurrently in the burning zone; this is significant in terms of the kinetics of clinkerization reactions and agglomeration processes. The exact temperature at which melt forms is determined on the chemical makeup of the feed.

### **2.5.2 Calcining**

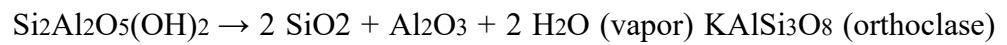
Calcite and other carbonate minerals are thermally decomposed to produce metallic oxides (mainly CaO) and carbon dioxide gas during the calcination process. By that, the kiln no longer has to execute the calcination function, the precalciner reduces kiln fuel usage.

### **2.5.3 Clinkering**

Because clinker is a complex combination of components, it necessitates a multi-staged heat treatment in the kiln. The kiln is where the majority of the clinker producing process takes place. The following are the steps of the kiln phase :-

- a) Evaporation of free water : A pressure greater than atmospheric is necessary to vaporise the water from the raw material slurry combination. When the temperature climbs over 120°C, water gets superheated and evaporation eventually ceases.
- b) Clay decomposition : "Clay" minerals, the most prevalent of which is kaolinite, Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, account for the majority of the alkalis in raw

materials. At high temperatures, the detached alkalis react with the acid fumes present in the kiln. The following are effective responses :



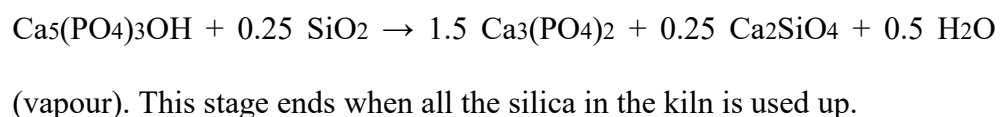
c) Decomposition of dolomite : The magnesia in the raw-mix occurs mostly as dolomite,  $\text{CaMg}(\text{CO}_3)_2$ , but also as silicate and carbonate. Dolomite reacts as follows :  $\text{CaMg}(\text{CO}_3)_2 \rightarrow \text{CaCO}_3 + \text{MgO} + \text{CO}_2$

Again, non-carbonate magnesium compounds (for example, phlogopite) react thus :  $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + 0.5 \text{SO}_2 + 0.25 \text{O}_2 \rightarrow 0.5 \text{K}_2\text{SO}_4 + 3 \text{MgO} + 0.5 \text{Al}_2\text{O}_3 + 3 \text{SiO}_2 + \text{H}_2\text{O (vapor)}$

d) Calcite breakdown at low temperatures Calcium carbonate, present in the raw-mix as calcite, emits carbon dioxide in quantities more than half the mass of the final clinker. This need a significant amount of heat. One of the parameters influencing production and heat consumption in the kiln is the efficiency of this reaction. At roughly 650°C, pure calcite in the kiln decomposes :  $2 \text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4 + 2 \text{CO}_2$

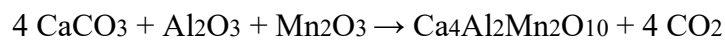
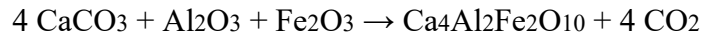
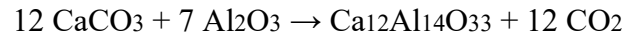
Surface tension draws reactive clay breakdown products and tiny quantities of alkali sulphate/chloride-melt together, acting as an ion transfer medium.  $\text{CO}_2$  is created here, but no free lime ( $\text{CaO}$ ) is made. Magnesium interacts with silica in the silicate phases to form forsterite (which solidifies as belite) :  $2 \text{MgO} + \text{SiO}_2 \rightarrow \text{Mg}_2\text{SiO}_4$

Phosphorus (as apatite in raw-mix) reacts with a little free silica and produces whitlockite (which also goes into solid solution in belite) :-



e) Alumina and iron oxide react : Calcium carbonate reacts with other oxides, but no free lime is generated. Though tricalcium aluminate is stable here, it appears that weakly crystallised mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) is generated.

The reactions at this stage are :-



f) Decomposition of residual calcite: At this step, a little quantity of calcite remains and creates free lime for the first time :  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$

g) After that, the mixture is sintered in a rotary kiln to make clinker. Sintering (or burning) is a thermochemical reaction triggered by the inhalation of hot combustion gases (1800-2000°C). Through a bypass, the kiln waste gases created by this process are evacuated. Sintering also the process of compacting and creating a solid mass of material to the point of liquefaction using heat or pressure without actually melting it. Clinker flux is formed when the temperature within the kiln hits around 1300°C (the eutectic melting point of aluminate, ferrite, and silicate). When the liquid is created, alite, which becomes stable at temperatures over 1250°C, begins to develop.

The principal reaction of this stage is as follows :-



The resulting liquid functions as a solvent for ion exchange between the solid phases while also drawing the reactant particles together via surface tension. The powdered or granular mixture immediately solidifies as clinker nodules.

Table 2.7 : List of process occur during clinkerization

Temperature range in °C.	Characteristic Processes	Type of Process
- 100	Drying, evaporation of free water	Endothermic
100 - 400	Elimination of absorbed water	Endothermic
400 - 750	Decomposition of clay minerals Kaolinite → metakaolinite	Endothermic
600 - 900	Decomposition of metakaolinite to free reactive oxides	Endothermic
600 - 1000	Decomposition of carbonates to free reactive oxides	Endothermic
800 - 1300	Combination of reactive oxides to form intermediate or final clinker minerals	Exothermic
1300 - 1380	Formation of clinker melt from aluminates and ferrites	Endothermic
1250 - 1500	Formation of Alite (C <sub>3</sub> S) - the principal clinker mineral	Endothermic

#### 2.5.4 Cooling

The clinker cooler is the final component of the pyroprocessing system. Clinker cooling is a crucial procedure in the manufacture of cement and improving the cooling effect can help lower the temperature of the clinker, recover waste heat, and create favourable circumstances for later cement handling, storage, or transportation. This production phase recovers up to 30% of the heat input to the kiln system, freezes minerals to lock in desired product characteristics, and allows the cooled clinker to be handled with standard conveyance equipment. The clinker is cooled from around 1100°C to 93°C (2000°F to 200°F) in these coolers by ambient air passing through the clinker and into the rotary kiln for use as combustion air. Lower clinker discharge temperatures are accomplished by circulating more air through the clinker in the reciprocating grate cooler. This extra air is either vented to the atmosphere, used to dry coal or raw materials, or used as a combustion air source for the precalciner because it can't be used in the kiln for efficient combustion. Clinker cooling is

required because it is difficult to convey the hot clinker, the grinding process is hampered by hot clinker, the recovered heat content of hot clinker, which is around 200 kcal/kg, is a major component in cutting manufacturing costs and cooling the cement properly increases its quality.

## **2.6 Clinker Hydration Reaction**

Clinker is anhydrous (devoid of water), having been produced in a hot kiln. If we ignore the small amount of water in any gypsum added during the clinker grinding stage, cement powder is also anhydrous. The reaction with water is known as "hydration." This involves a variety of reactions, many of which occur concurrently.

The highly reactive Portland cement clinker powder can be mixed with water to produce a final hardened material via a complex series of reactions known as the hydration process, which involves crystal phase dissolution, surface reactions, gel formation, precipitation of new phases, and textural changes. The reactivities of the various crystal phases present in clinker vary greatly, with C<sub>3</sub>A having the highest and C<sub>2</sub>S having the lowest. In fact, C<sub>3</sub>A is so exothermally reactive that it can cause the paste to set too quickly (flash set), resulting in a loss of workability. As a result, as a set-controlling agent, a calcium sulphate material (typically gypsum, but also bassanite and/or soluble anhydrite) is usually interground with the clinker in the range of 4% to 8% by mass. The finely powdered clinker-gypsum mixture is marketed as standard Portland cement (PC, also known as ordinary Portland cement), which is then mixed with water. The mass ratio of water to cement, w/c, typically ranges from 0.3 to 0.5, though enough water to fully react with cement would necessitate w/c of 0.38 or higher. When we add an aggregate material to the paste, we get mortar (fine aggregate,