EFFECT OF WASTE GYPSUM FROM CERAMIC SLIP CASTING MOULD ON THE PROPERTIES OF PORTLAND CEMENT

by

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Saya isytiharkan bahawa kandungan yang dibentangkan di dalam tesis ini adalah hasil kerja saya sendiri dan telah dijalankan di Universiti Sains Malaysia kecuali dimaklumkan sebaliknya. Tesis ini juga tidak pernah disertakan untuk ijazah yang lain sebelum ini.

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LIST OF ABBREVIATION

AFm	:	Monosulfate
AFt	:	Ettringite
AR	:	Aluminate Ratio
C-S-H	:	Calcium Silicate Hydrate
C_3A	:	Tricalcium aluminate, aluminate
C_4AF	:	Tetracalcium aluminoferrite, Ferrite
CL	:	Clinker
CMNG	:	Cement from the grinding of clinker with natural gypsum in various proportions from 3% to 6% in a laboratory ball mill for 90 minutes.
CMWG	:	Cement from the grinding of clinker with Waste gypsum in various proportions from 3% to 6% in a laboratory ball mill for 90 minutes.
CMWG-2	:	Cement from the grinding of clinker with Waste gypsum in various proportions from 3% to 6% in a laboratory ball mill for 120 minutes.
C_2S	:	Dicalcium silicate, Belite
C_3S	:	Tricalcium silicate, Alite
DSC/Tg	:	Differential Scanning Calorimetry / Thermogravimetry
FESEM	:	Field Emission Scanning Electron Microscopy
FGD	:	Flue Gas Desulfurization
LOI	:	Loss On Ignition
LSF	:	Lime Saturation Factor
NG	:	Natural Gypsum

SR	:	Silica Ratio
VRM	:	Vertical Roller Mills
WG	:	Waste Gypsum
XRD	:	X-Ray Diffraction
XRF	:	X-Ray Fluorescence

EFFECT OF WASTE GYPSUM FROM CERAMIC SLIP CASTING MOULD ON THE PROPERTIES OF PORTLAND CEMENT

ABSTRACT

The aim of this work is to investigate the possibility of using waste gypsum ($CaSO_4.2H_2O$) which is the waste material from the hydration of plaster of Paris in ceramic factory as a replacement or alternative material to natural gypsum ($CaSO_4.2H_2O$) in cement production. Prior to cement grinding test work, the raw materials such as clinker, natural gypsum and waste gypsum had been characterized using X-Ray Diffraction, X-Ray Fluorescence, Differential Scanning Calorimetry / Thermogravimetry and Field Emission Scanning Electron Microscopy. For cement grinding test work, clinker was ground with natural gypsum in differents proportion from 3% to 6% in laboratory ball mill for 90 minutes and the same process had been repeated with waste gypsum for 90 minutes and 120 minutes to produce Portland cement with a specific surface area of around 3500 cm^2/g with tolerance ± 10%. All cement samples were tested by determining the chemical composition, phases, fineness, setting time, expansion, strength and heat of hydration. From the results, it showed that waste gypsum still contained some amount of plaster of Paris (hemihydrate) which had not converted to gypsum (dihydrate). The amount of hemihydrate in waste gypsum caused cement to set faster but did not have positive effect on the strength (about 50MPa) at the age of 28 days. It could be concluded that waste gypsum could be possibly used as a replacement or alternative material to natural gypsum in cement production, especially at level of 4% gypsum addition with both types of gypsum exhibiting almost the same properties of cement such as setting time and strength.

KESAN SISA GIPSUM DARIPADA ACUAN TUANGAN SLIP SERAMIK TERHADAP SIFAT-SIFAT SIMEN PORTLAND

ABSTRAK

Tujuan kajian ini dijalankan adalah untuk mengkaji kemungkinan menggunakan sisa gipsum yang merupakan bahan terbuang daripada pengeringan plaster Paris dalam kilang seramik sebagai bahan ganti atau bahan alternatif untuk gipsum semulajadi dalam pembuatan simen. Sebelum kajian pengisaran simen, bahan mentah seperti klinker, gipsum semulajadi dan sisa gipsum telah dicirikan dengan menggunakan Pembelauan Sinar X, Pendarfluor Sinar X, Permeteran Kalori Pengimbasan Kebezaan/Permeteran Graviti Haba dan Mikroskop Elektron Imbasan. Untuk ujian pengisaran simen, klinker telah dikisar bersama gipsum semulajadi dengan perkadaran 3% hingga 6% dalam pengisar bebola makmal selama 90 minit. Proses yang sama diulang dengan menggunakan sisa gipsum selama 90 minit dan 120 minit untuk menghasilkan simen Portland dengan luas permukaan spesifik dalam lingkungan 3500 cm^2/g dengan ±10% kelegaan. Semua produk simen diuji dengan menentukan komposisi kimia, fasa-fasanya, kehalusan, masa pensetan, pengembangan, kekuatan dan kadar pengeringan haba. Daripada keputusan yang diperolehi, menunjukkan sisa gipsum masih mengandungi sejumlah plaster Paris (hemihidrat) yang belum bertukar kepada gipsum (dehidrat). Kandungan hemihidrat dalam sisa gipsum menyebabkan simen menjadi keras dengan cepat tetapi tidak memberi kesan yang positif pada kekuatan (50MPa) simen pada hari ke 28. ini membuktikan kemungkinan sisa gipsum boleh digunakan sebagai bahan ganti atau bahan alternatif kepada gipsum semulajadi dalam pembuatan simen terutamanya pada 4% penambahan gypsum di mana kedua-dua jenis gipsum menunjukkan sifat-sifat simen yang hampir serupa seperti masa pensetan dan kekuatan.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Portland cement is a manufactured product made by blending different raw materials and firing them at a high temperature in order to achieve precise chemical proportions of calcium, silica, alumina and iron in the finished product, known as cement clinker. Clinker typically has a composition in the region of 67% CaO, 22% SiO_2, 5% Al_2O_3, 3% Fe_2O_3 and 3% of other components [Taylor, 1997]. Therefore, cement is essentially a mixture of calcium silicates and smaller amounts of calcium aluminates that react with water and cause the cement to set. The requirement for calcium is met by using high calcium limestone (or its equivalent calcareous raw material) and clay, mudstone or shale as the source of most of the silica and alumina. Finished cement is produced by finely grinding together around 95% of cement clinker with 5% gypsum (or anhydrite) which helps to retard the setting time of cement.

The quality of cement clinker is directly related to the chemistry of the raw materials used. Around 80-90% of raw material for the kiln feed is limestone. Clayey raw material accounts for between 10-15%, although the precise amounts will vary. Magnesium carbonate, which may be present in limestone, is the main undesirable impurity; the level of magnesia (MgO) in the clinker should not exceed 4%, because quantities of this component in excess of about 2% can slow the reaction with water and cause destructive expansion of hardened concrete. Free lime can behave similarly. Excessive contents of SO_3 can also cause expansion, and upper limits, typically is around 3.5% for ordinary Portland cement. Alkalis (Na_2O and K_2O) can undergo expansive reactions with certain aggregates, and some specifications limit the content to 0.6% [Taylor, 1997].

Beside Portland cement, there are other types of cement called blended cement. Blended cement is produced by finely grinding Portland cement clinker with other constituents, such as blast furnace slag, natural pozzolanas, silica fume, metakaolin, siliceous fly ash, calcareous fly ash, limestone fine and shale. According to BS EN 197-1 standard, there are five main types of cement used for concrete (Table 1.1) [British Geological Survey, (2004)].

Table 1.1 Type of cement for concrete according to EN 197-1 [British Geological Survey, (2004)]

CEM I Portland cement	Comprising of Portland cement and up to 5% of minor additional constituents.
CEM II Portland-composite cement	Comprising of Portland cement and up to 35% of other single constituents.
CEM III Blastfurnace cement	Comprising of Portland cement and higher percentages of blastfurnace slag
CEM IV Pozzolanic cement	Comprising of Portland cement and higher percentages of pozzolana
CEM V Composite cement	Comprising of Portland cement and higher percentages of blastfurnace slag and pozzolana or fly ash.

1.2 World Cement Production

According to European Cement Association (Cembureau), world production of cement rose steadily from 1997 to 2003 (Figure 1.1), increasing by almost 436 millions tons during this period [JCA, 2005]. According to United States Geological Survey, Mineral Resources Program, it was estimated that cement production in 2004 was

around 2130 million tons. This was consistent with improving economic conditions and population growth in many parts of the world [Index mundi, 2007].

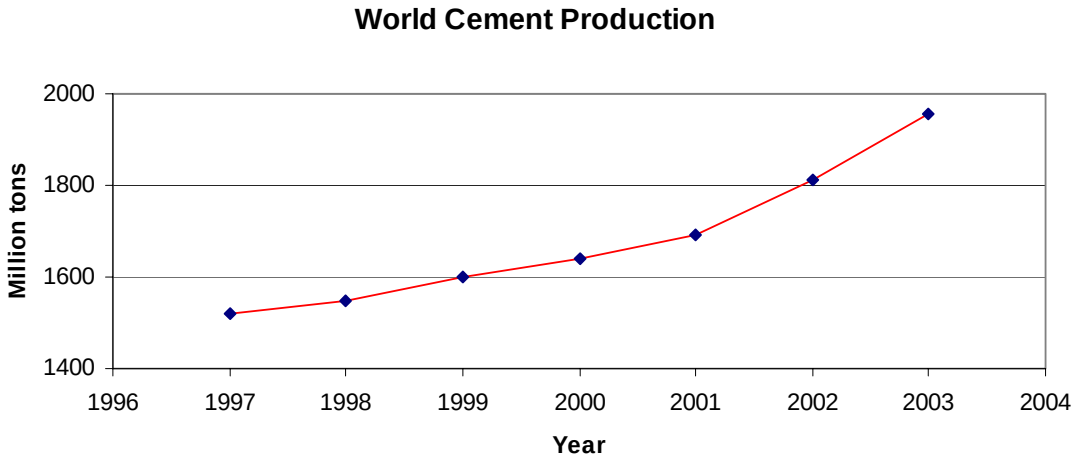

Figure 1.1: World cement production 1997 – 2003 [JCA, 2005]

Recent economic growth in China has stimulated growth in its construction industry, with the result that China's cement production formed 43.94% of the world's total production in 2003. Actual Chinese cement production increased from 578 million tons to 859 millions tons over the period 2000-2003 (Figure 1.2), with an increase of 32.71% [JCA, 2005]. It is clear that cement production is a function of population and economic growth, both at country and world scales. With the global population expected to rise to over 9.2 billion in 2050 [UN, 2007] further growth in world cement production can be expected.

Malaysia is a developing country and the demand for cement is increasing with increasing demand for new schools, hospitals, offices, shops and infrastructure development. According to the report by United States Geological Survey, Mineral Resources Program, the Malaysian cement production has increased from 11.445 million tons in 2000 to 18 million tons in 2004 (Figure 1.3) [Index Mundi, 2007]. It shows that the cement production increases with the growth of the construction industry.

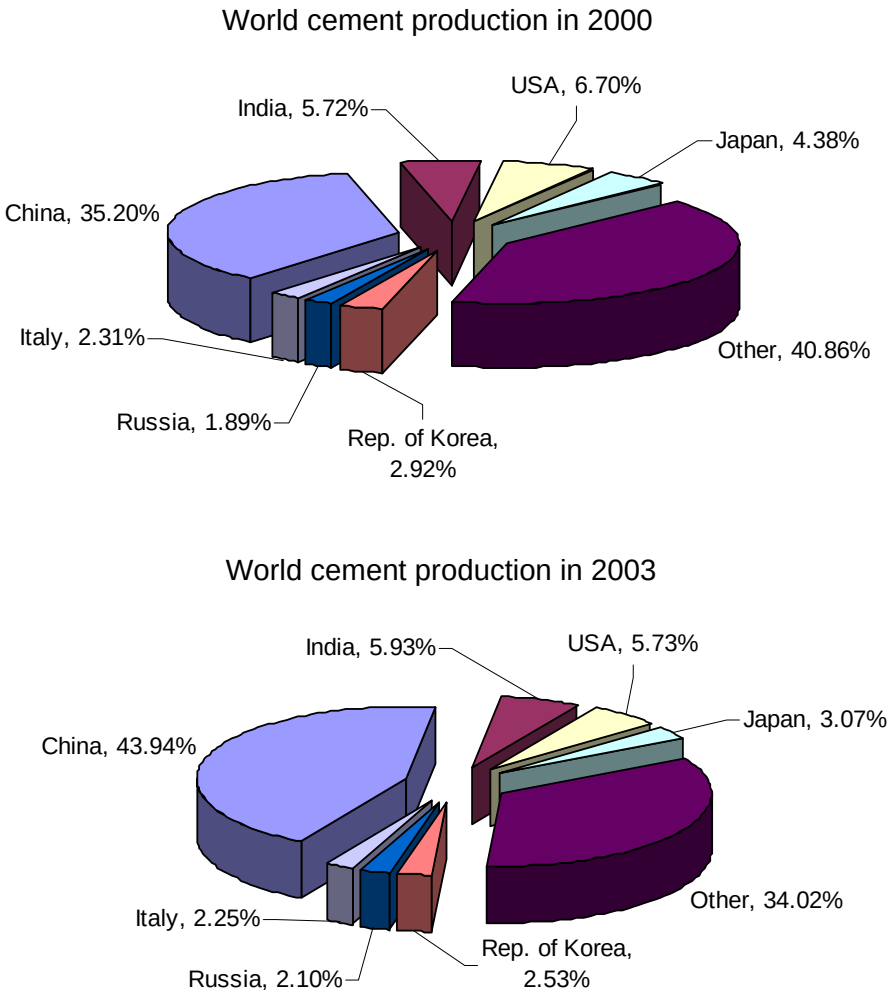

Figure 1.2 World cement production in 2000 and 2003 [JCA, 2005]

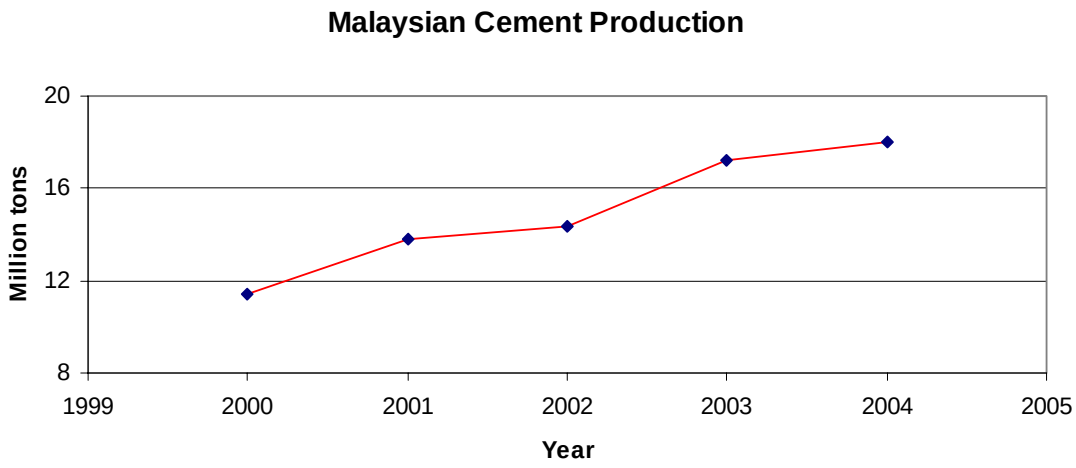

Figure 1.3: Malaysian cement production 2000 – 2004 [Index Mundi, 2007]

1.3 The Role of Gypsum in Cement

Gypsum is a natural mineral which has the formula $CaSO_4.2H_2O$. Gypsum is a soft, transparent or translucent mineral composed of crystallized calcium sulphate ($CaSO_4$), found naturally primarily in sedimentary deposits. It is used in the manufacture of wall boards, paper, paints, plasters and cement. According to Gypsum Recycling International (2007), in total 80 million tons of plasterboard, wallboard and drywall is produced every year.

Gypsum is not a raw material in the kiln feed but is added to clinker at the cement grinding stage of Portland cement to regulate extreme setting reaction which occurs in the presence of water [Bye, 1999], usually at the level of 5% which is equal to approximately 2.1% of SO_3. The gypsum content of cement is expressed in terms of its sulphate (SO_3) content. The maximum SO_3 content allowed by European Standard ENV 197-1: 1992 is 3.5%. The setting of cement is primarily due to the reaction of tricalcium aluminate (C_3A), $3CaO.Al_2O_3$. The reaction of pure C_3A with water is created in the form of interlinking bridge of solid material between the cement particles. These interlinking bridges reduce the mobility of the cement particles and produce a firm structure that leads to immediate stiffening of the paste, known as flash set. To prevent this from happening, gypsum is added to cement clinker to retard the setting of cement. Gypsum and C_3A react to form insoluble calcium sulfoaluminate ($3CaO.Al_2O_3.3CaSO_4.32H_2O$), called ettringite ((AFt) (Equation 1.1). When gypsum is dropped and C_3A remains, ettringite will react with C_3A to form $3CaO.Al_2O_3.CaSO_4.12H_2O$, called monosulfate (AFm) (Equation 1.2).

$$C_3A + 3(CaSO_4.2H_2O) + 26H_2O \longrightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O$$

(Equation 1.1)

$$3CaO.Al_2O_3.3CaSO_4.32H_2O + 2C_3A + 4H_2O \longrightarrow 3(3CaO.Al_2O_3.CaSO_4.12H_2O)$$

(Equation 1.2)

Gypsum does not only react with C_3A, but it also reacts with C_4AF to form calcium sulfoferrite as well as calcium sulfoaluminate, and its presence may accelerate the hydration of the silicates [Neville, 2002]. As well as influencing the setting time, gypsum also has an influence on other properties of cement. The more important of these are strength development. The addition of gypsum to cement increases the strength and reduces shrinkages. However, the addition of excessive amounts of gypsum will cause expansion to occur, which is why cement standards place limit on the sulphate content. Gypsum also influences the grinding ability of cement, which is the grinding energy required to produce cement. Grinding aids such as diols (glycols) or triethanolamine at levels of about 0.1% have been found to reduce the energy needed in milling to reach a given fineness. Gypsum is more easily ground than clinker and sometimes referred to as a grinding aid, possibly only because it is softer than clinker [Bye, 1999].

Dehydration of gypsum, $CaSO_4.2H_2O$ (dihydrate), occurs at relatively low temperature from 100^0C to 160^0C. Such temperatures can occur during the cement grinding process and result in the formation of significant quantities of $CaSO_4.0.5H_2O$ (hemihydrate) and $CaSO_4$ (anhydrite). The ratios in which these calcium sulphates formed in cement can have a profound effect on the setting behavior, because their respective solubilities in water are significantly different from one another. Upon mixing with water, hemihydrate and anhydrite react readily with water to form needle-shape crystals of gypsum. This leads to gypsum precipitation and some rigidity or stiffening of the concrete or mortar, making it necessary to add more water for workability and resulting in a lowering of the strength properties. This process is referred to as “False Setting". The dihydrate form is the preferred form required in cement [Strydom and

Potgieter, 1999]. Thus, this requires controlling the temperature inside the mill during the grinding process of clinker and gypsum.

1.4 Problem statement

In the cement industry, natural gypsum ($CaSO_4.2H_2O$) is ground with clinker during production of Portland cement to delay the rapid reaction between C_3A and water and to regulate cement setting properties. The required amount of gypsum in a type of cement increases with the amount of C_3A in the clinker and also depends on its purity. Instead of gypsum, other forms of calcium sulfate can be used in the manufacture of cement such as hemihydrate ($CaSO_4.0.5H_2O$) and anhydrite ($CaSO_4$) [Neville, 2002]. Natural gypsum may contain anhydrite as impurity, at levels which vary widely with source. Gypsum which is too rich in natural anhydrite is unsuitable for use alone because this mineral dissolves too slowly in water to retard setting sufficiently.

In some countries, because of the lack of gypsum deposits or due to environmental concerns, chemical gypsums may be employed as by-products. However, the use of by-products depends on their not being too contaminated by residues of the product of the chemical process which will affect the setting and/or hardening of concrete. FGD gypsum is industrial by-product derived from flue gas desulfurization process [Tzouvalas et al, 2004b]. The chemical reactions that can take place to convert flue gases into gypsum are shown in Equations 1.3, 1.4 and 1.5:

$$SO_2 + H_2O \longrightarrow H^+ + HSO_3^- \qquad \text{(Equation 1.3)}$$

$$H^+ + HSO_3^- + 0.5O_2 \longrightarrow 2H^+ + SO_4^{-2} \qquad \text{(Equation 1.4)}$$

$$2H^+ + SO_4^{-2} + Ca(OH)_2 \longrightarrow CaSO_4.2H_2O \qquad \text{(Equation 1.5)}$$

Beside FGD gypsum, there are other by-products gypsum that have been used in cement manufacture such as phosphor-, citro-, desulpho- and boro-gypsum as setting retarders [Ozkul, 2000; Papageorgiou et al, 2005; Kavas et al, 2005]. These by-products come from the chemical reaction and result in gypsum ($CaSO_4.2H_2O$) which has similar chemical composition to natural gypsum. That is the reason why these by-products can be used to replace natural gypsum in cement manufacture.

On the other hand, in ceramic factory, plaster of Paris has been used as the mould for slip casting technique. The hydration of plaster of Paris also results in gypsum ($CaSO_4.2H_2O$) which has similar chemical composition to natural gypsum and also by-product gypsum. The chemical reactions that can take place to convert plaster of Paris into gypsum are described as follows:

When gypsum ($CaSO_4.2H_2O$) is heated to a temperature of about 150^0C, it will lose about three quarters of its water to form calcium sulfate hemihydrate ($CaSO_4.0.5H_2O$) (Equation 1.6) and when it is ground into the powder form, is termed as Plaster of Paris (POP).

$$CaSO_4.2H_2O \longrightarrow CaSO_4.0.5H_2O + 1.5H_2O \qquad \text{(Equation 1.6)}$$

In the ceramic factory, POP is used as the mould to produce ceramic product in slip casting technique. When POP is mixed with water, it is converted into gypsum (Equation 1.7) [GPDA 2005; Kotz et al, 2003].

$$CaSO_4.0.5H_2O + 1.5H_2O \longrightarrow CaSO_4.2H_2O \qquad \text{(Equation 1.7)}$$

After about 1000 casting, these POP moulds can no longer be used, therefore they become waste materials, named as waste gypsum (WG). Based on the high

sulphate content of waste gypsum's mineralogical phases, there are possibilities of replacing natural gypsum with waste gypsum as by-product in cement manufacture.

1.5 Objective

The main objective of this work is to study the effect of waste gypsum (WG) as a replacement for natural gypsum (NG) on the quality of Portland cement. The raw materials used were characterized using various methods such as XRD, XRF, DSC/Tg and SEM. Natural and waste gypsum were added to clinker at 3-6% to produce cement with specific surface area of about 3500cm^2/g with tolerance ± 10%. The cement products were tested for chemical composition, phases, fineness, setting time, expansion, strength and heat of hydration. It is hoped that the outcome of this research would lead to a better understanding of the properties of waste gypsum and its possibility as an alternative material to natural gypsum in cement production.

1.6 Scope of Research

The scope of research is designed to cover the three essential elements such as characterization of raw materials, grinding work, and determining of properties and quality of cement product using natural gypsum and waste gypsum:

i. The properties of waste gypsum and natural gypsum will be characterized in terms of their chemical composition, mineral compound, morphology, microstructure, and particles size.

ii. The final product, cement, will be characterized in terms of surface area, percent passing 45µm and particle size distribution to study the effect of waste gypsum on grinding ability of Portland cement.

iii. The properties of cement will be characterized in terms of chemical composition, morphology, microstructure, setting time, expansion, heat of hydration, compressive and flexural strength to study the effect of waste gypsum on quality of Portland cement.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The process of manufacture of Portland cement (Figure 2.1) consists essentially of grinding the raw materials, mixing them intimately in certain proportions and burning in a large rotary kiln at a temperature of up to about 1450 ^{0}C, and the clinker is formed when the material sinters and partially fuses into balls. The clinker is cooled and ground to a fine powder, with some gypsum added, and the resulting product is the commercial Portland cement so widely used throughout the world [Neville, 2002].

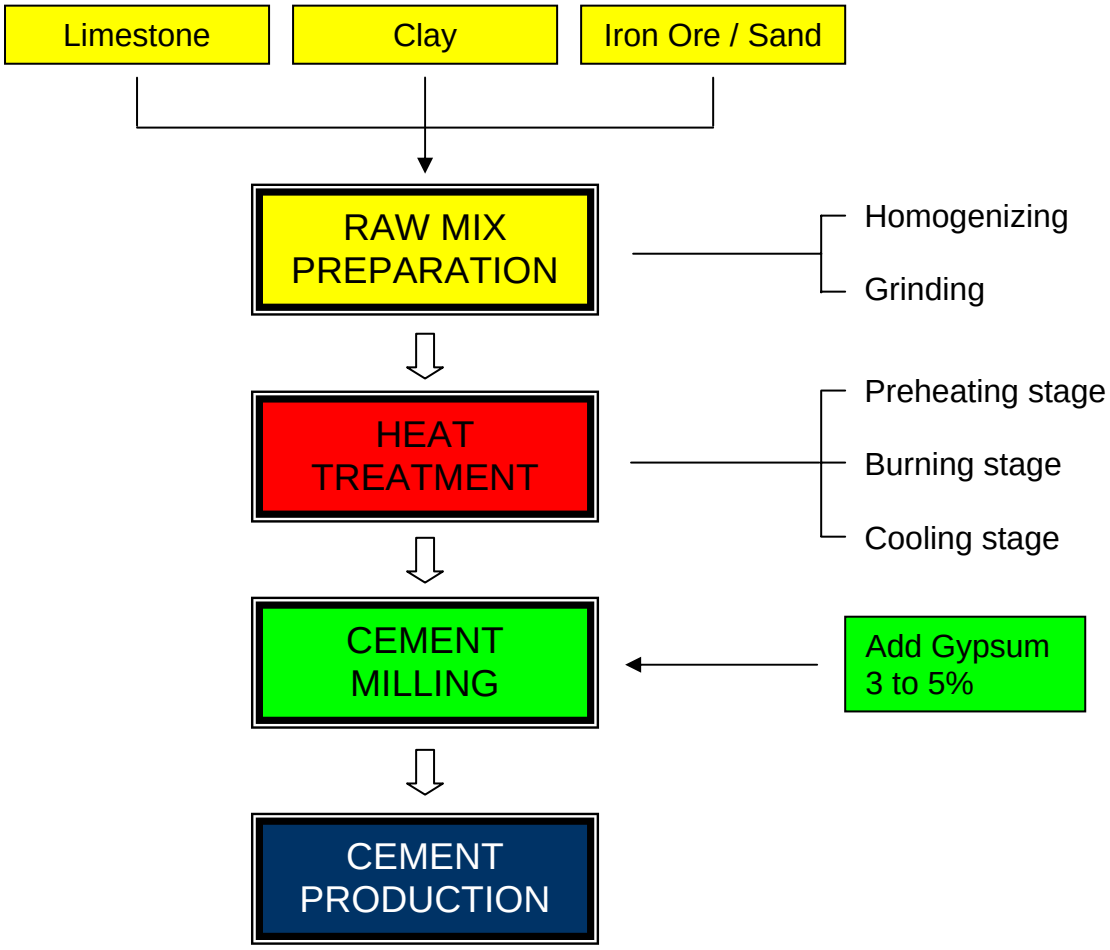

Figure 2.1: Main processes in the manufacture of Portland cement

2.1.1 Raw Mix Preparation

Portland cement consists principally of compounds of calcium and silica with smaller amounts of aluminum and iron compounds. There are made from homogeneous, balanced mixtures of calcareous and argillaceous materials. Chalk or limestone is generally used as the calcareous component and clay or shale as the argillaceous component, but such is the simplicity of their raw materials requirement that Portland cement can be manufactured from any materials which will provide the required balance of compound-forming constituents [Eglinton, 1987].

The mixing and grinding of the raw materials can be done either in water or in a dry condition; hence the names “Wet process” and “Dry process”. The actual methods of manufacture depend also on the hardness of the raw materials used and on their moisture content [Neville, 2002].

2.1.2 Heat Treatment

The raw materials are ground finely and blended to produce the raw meal. The raw meal is fed at the top of the preheater tower and passes through a series of cyclones in the tower (Figure 2.2). About 85%-95% of the raw meal is heated to 1000^0c extremely quickly, “calcining” the calcium carbonate in limestone to calcium oxide before being fed into a rotary kiln. In the rotary kiln tube, the feed moves slowly as the tube rotates. When the meal passes through the burning zone, it reaches clinkering temperatures of about 1400^0C - 1500^0C. Nodules form as the burning zone is approached. When the clinker has passed the burning zone, it starts to cool at the end of the kiln and drops out into the cooler [Understand cement, 2002].

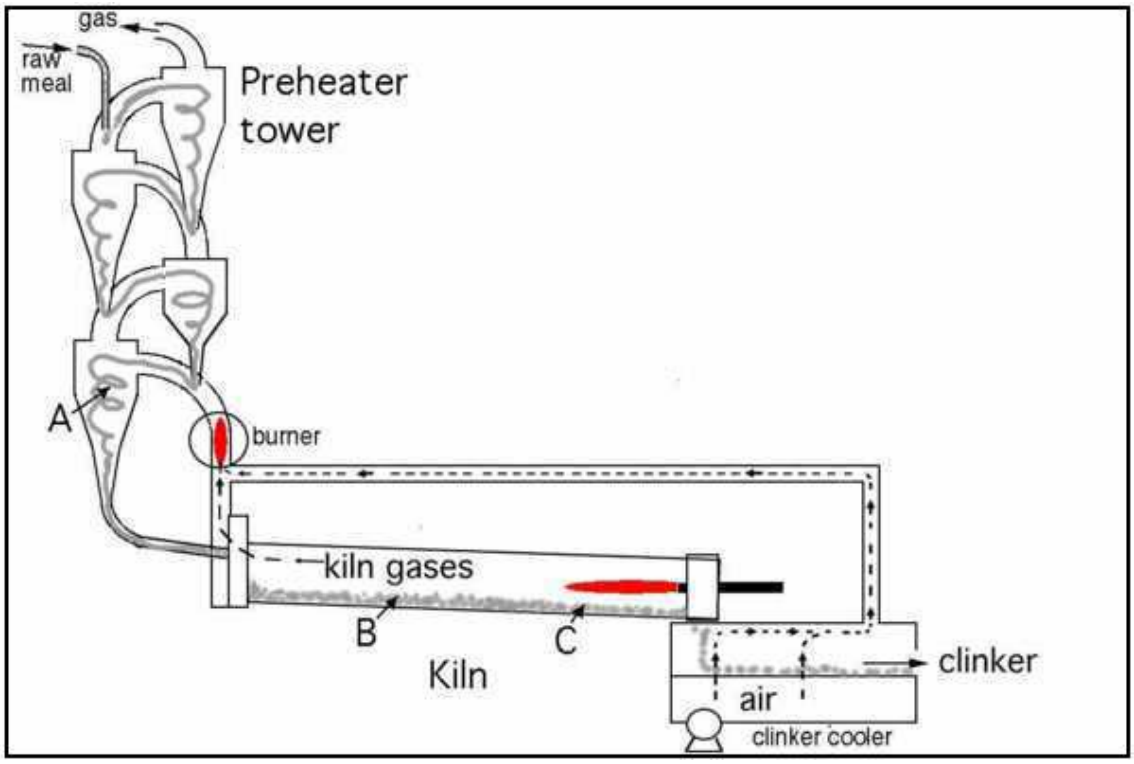

Figure 2.2: Kiln and preheater tower. At 'A,' the raw meal largely decarbonates; at 'B,' the temperature is 1000 ^{0}C - 1200 ^{0}C and intermediate compounds are forming and at 'C,' the burning zone, clinker nodules and the final clinker minerals form [Understand cement, 2002].

2.1.3 Cement milling

After it leaves the cooler, clinker is conveyed to a covered store. A quantity (2-8%, but typically 5%) of calcium sulfate (usually gypsum or anhydrite) is added to the clinker and the mixture is finely ground to form the finished cement powder, usually in the ball mill, with desired surface area or particle size distribution. To achieve the controlled particle size distribution and surface area, it is necessary to use high efficiency classifiers in closed circuit grinding of clinker. Then, cement is conveyed by belt or powder pump to a silo for storage. The cement is delivered to end-users either in bags or as bulk powder blow from a pressure vehicle into the customer's silo.

2.2 Clinker

Portland cement is made primarily from a calcareous material, such as limestone or chalk, and from alumina and silica found as clay or shale. The process of

manufacture of cement consists essentially of grinding the raw materials, mixing them intimately in certain proportions and burning in a large rotary kiln at a temperature of up to about 1450 ^{0}C when the material sinters and partially fuses into balls known as Clinker [Neville, 2002].

2.2.1 Control Factors

We can not make cement if we don't know all about the raw materials. The raw materials are blended in a way of determining the quantities of oxide compositions contained such as CaO, SiO_2, Al_2O_3 and Fe_2O_3. The composition and reactivity of the minerals used will determine clinker characteristics. There are three parameters that can be used to ensure that the finished product meets the specifications of the type of Portland cement to be made. These include: LSF (lime saturation factor), SR (silica ratio), AR (alumina ratio).

Lime saturation factor: The formula of lime saturation factor (Equation 2.1) is derived from the plane of 100% lime saturation in the quaternary (C-S-A-F) which makes possible the calculation of the lime required for saturation of the other oxides at the clinkering temperature.

$$\mathbf{LSF = CaO / (2.8\ SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3)} \quad \text{…….(Equation 2.1)}$$

LSF is a ratio of CaO to the other three main oxides. It controls the ratio of alite to belite in the clinker. The clinker with a higher LSF will have a higher proportion of alite to belite than the clinker with low LSF which results in increasing the grinding ability and also it will make the raw mix more difficult to burn [Erik, 1994; Kristen, 1993]. Typical LSF values in modern clinkers are 0.90 - 0.98. Values above 1.0 indicate that free lime is likely to be present in the clinker. This is because, in principle, at LSF=1.0,

all the free lime should have combined with belite to form alite. If the LSF is higher than 1.0, then surplus free lime occur.

Silica ratio: A high silica ratio means that more calcium silicates are present in the clinker and less aluminate and ferrite. SR is typically between 2 and 4. Increase in SR makes the clinker more difficult to burn [Taylor, 1997]. The SR levels that govern the amount of liquid will also affect the alite crystal size. A higher SR implies less liquid and will result in larger alite crystal size [Erik, 1994]. The silica ratio (Equation 2.2) is defined as:

$$\mathbf{SR = SiO_2 / (Al_2O_3 + Fe_2O_3)} \quad \text{…….(Equation 2.2)}$$

Alumina ratio: This determines the potential relative proportions of aluminate and ferrite phase in the clinker. An increase in clinker AR means there will be proportionally more aluminate and less ferrite in the clinker. In ordinary Portland cement clinker, the AR is usually between 1 and 4. The alumina ratio (Equation 2.3) is defined as:

$$\mathbf{AR = (Al_2O_3) / (Fe_2O_3)} \quad \text{…….(Equation 2.3)}$$

2.2.2 Reaction of Clinker Formation

In the manufacture of Portland cement clinker, the raw materials, typically limestone and clay or shale, are mixed and heated to a temperature of about 1450 ^{0}C in the kiln. The reactions which take place in the kiln can be conveniently divided into three groups [Taylor, 1997], as follows:

2.2.2.1 Decomposition of Raw Materials

Decomposition of raw materials (reactions at temperatures up to about 1300 ^{0}C) which include: The decomposition of calcite (calcining), the decomposition of clay minerals, and reaction of calcite or lime formed from it with quartz and clay mineral decomposition products. The initial silicate product is belite. Some calcium aluminate and ferrite phases also start to form. Liquid is formed only to a minor extent at this stage, but may have an important effect in promoting the reactions. At the end of this stage, the major phases present are belite, lime, aluminate and ferrite. The last two may not be identical with the corresponding phases in the final product.

2.2.2.2 Clinkering (Reaction at 1300 ^{0}C to 1450 ^{0}C)

A melt is formed, mainly from the aluminate and ferrite, and by 1450 ^{0}C some 20 to 30% of the mix is liquid. Much of the belite and nearly all the lime react in the presence of the melt to give alite. The material is nodulised to form the clinker.

2.2.2.3 Reactions during Cooling

During cooling, the liquid crystallizes, giving mainly aluminate and ferrite. Polymorphic transition of the alite and belite occur.

2.2.3 Chemical Composition of Clinker

Typically, clinker consists four main phases such as:

i. Alite or tricalcium silicate, C_3S ($3CaO.SiO_2$)
ii. Belite or dicalcium silicate or, C_2S ($2CaO.SiO_2$)
iii. Tricalcium aluminate or aluminate, C_3A ($3CaO.Al_2O_3$)
iv. Calcium alumino-ferrite, or tetracalcium aluminoferrite or ferrite, C_4AF ($4CaO.Al_2O_3.Fe_2O_3$)

Bogue Calculation

The standard Bogue calculation refers to cement clinker, rather than cement, although it can be adjusted for use with cement. This is a very commonly-used calculation in the cement industry. The general solution to the calculation is expressed in Equations 2.4, 2.5, 2.6 and 2.7 [Bye, 1999].

$$C_4AF = 3.04\ Fe_2O_3 \quad \text{…….(Equation 2.4)}$$

$$C_3A = 2.65\ Al_2O_3 - 1.69\ Fe_2O_3 \quad \text{…….(Equation 2.5)}$$

$$C_2S = 8.6\ SiO_2 + 1.08\ Fe_2O_3 + 5.07\ Al_2O_3 - 3.07\ CaO \quad \text{…….(Equation 2.6)}$$

$$C_3S = 4.07\ CaO - 7.6\ SiO_2 - 1.43\ Fe_2O_3 - 6.72\ Al_2O_3 \quad \text{…….(Equation 2.7)}$$

The calculation is simple in principle:

i. Firstly, according to the assumed mineral compositions, ferrite phase is the only mineral to contain iron. The iron content of the clinker therefore fixes the ferrite content.

ii. Secondly, the aluminate content is fixed by the total alumina content of the clinker, minus the alumina in the ferrite phase. This can now be calculated, since the amount of ferrite phase has been calculated.

iii. Thirdly, it is assumed that all the silica is present as belite and the next calculation determines how much lime is needed to form belite from the total silica content of the clinker. There will be a surplus of lime.

iv. Fourthly, the lime surplus is allocated to the belite, converting some of it to alite.

2.2.4 Microscopy of Clinker

Microscopy is a very powerful technique for examining cement clinker. Every stage of the cement manufacturing process can be improved through the use of a microscope. Some cement manufacturers use microscopy as a technique for kiln control, with clinker samples being examined continuously. A photographic microscope (Figure 2.3) is used to examine cement clinker and related materials. Specimens are usually prepared as polished sections or as powder mounts. Important characteristics that the microscope examines are [Campbell, 1999]:

i. Overall nodule microstructure - dense, porous, dense micronodules interconnected by tenuous 'bridges'. This gives a broad relative indication of burning conditions.
ii. Alite crystal size – Alite crystal size is an average of measurements on approximately 10 selected crystals. Typically, alite crystal sizes range from 25 to 65µm. Coarse alite may indicate a slow heating rate, excessive burning or coarse silica in the raw feed; silicate reactivity may be lower than it could be with improved burning conditions. Alite size of less than 15µm in 1000 tons per day kiln can be indicative of poor burning; a 20µm alite size is typical of poor burning in 4000 tons per day kiln. A well burned clinker (Free CaO < 0.6%) does not have alite crystals under 20µm [Campbell, 1999].
iii. Belite crystal size - larger belite crystals suggest longer time in the burning zone. Belite size range from 25 to 40µm is indicative of long burning time and belite size less than 10µm is typical of short burning time [Campbell, 1999].
iv. Aluminate and ferrite crystal size - coarse flux phases suggest slow cooling; finer, intergrown, flux phases indicate faster cooling.

v. Belite color also indicates the cooling rate; fast-cooled crystals are clear while slower cooling allows impurities to crystallize out along lattice planes imparting a yellow color.

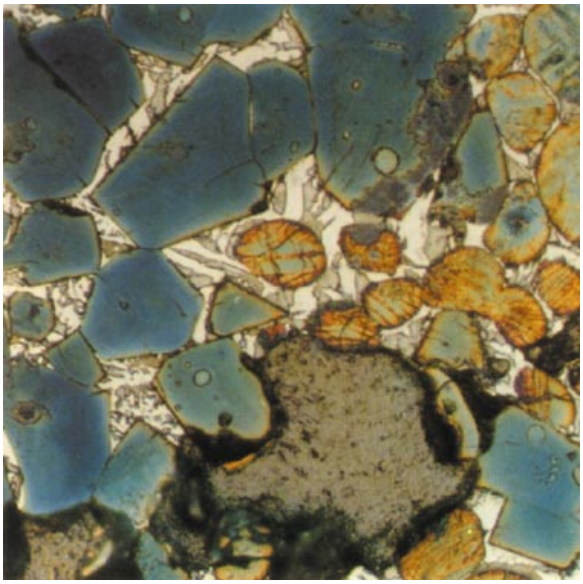

Figure 2.3:
Photograph of Polished section (Nital on KOH etch) of Portland cement. Blue alite C_3S, round tan to brown belite C_2S, matrix dark aluminate C_3A and brightly reflection ferrite C_4AF (Campbell, 1999).

2.3 Gypsum in Cement

In the cement industry, gypsum is added to clinker at the cement grinding stage in order to delay the rapid reaction between C_3A and water. The reaction of pure C_3A with water is created in the form of interlinking bridge of solid material between the cement particles. These interlinking bridges reduce the mobility of the cement particle and produce a firm structure that leads to immediate stiffening of the paste, known as flash set [Neville, 2002]. Gypsum is added to the clinker, usually at a level of 3 to 5%, depending on its purity. The gypsum content of cement can be expressed in terms of its sulphate (SO_3) content. The maximum SO_3 content allowed by European Standard ENV 197-1: 1992 is 3.5%. Bye (1999) said that the required addition of gypsum is typically taken as that which produces the highest 28 days concrete strength determined by standard procedure. The experimentally found optimum SO_3 is dependent on the chemistry of the clinker so that the level in commercial cement varies with source, an upper limit being set to protect consumers from excessive addition. Too

high level introduces a risk of concrete volume instability caused by the formation of the sulfoaluminate, ettringite, after the concrete has hardened [Bye, 1999].

Gypsum may contain anhydrite, and clay, quartz and calcite as impurities, at levels which vary widely with source. Deposit may be mined or quarried and separation of the purest materials is necessary for white cement. A materials too rich in natural anhydrite (> about 70%) is unsuitable for use alone because this mineral dissolves too slowly in water to retard setting sufficiently [Bye, 1999]. With the identical amount of SO_3, cements with anhydrite set faster than those with gypsum. It is evident that the addition of anhydrite accelerates the setting of cement. The faster setting of anhydrite is caused by the increasing amount of $CaSO_4$ in the admixture [Tzouvalas et al, 2004a].

Gypsum is more easily ground than clinker and sometimes referred to as a grinding aid, possibly only because it is softer than clinker. Iglesias (1999) also studied the grindinability of mixtures of 95% clinker and 5% gypsum with two different kinds of gypsum (similar chemical composition but different source), and it resulted in grinding power consumption differences of up to 15% [Iglesias et al, 1999].

2.3.1 By-Product Gypsum

In some countries, because of the lack of gypsum deposits or due to environmental concerns, chemical gypsums may be employed. These are by-product gypsum, such as phosphor-, citro-, desulpho-, boro- and FGD gypsum as setting retarders [Ozkul, 2000; Papageorgiou et al, 2005; Kavas, 2005; Tzouvalas, 2004b]. However, the use of these by-products depends on their not being too contaminated by residues of a product of the chemical process which will affect the setting and/or hardening of a concrete.

Desulphogypsum, from desulphurisation process in coal-burning plants, and citrogypsum, a by-product of citric acid production, are other important sources of chemical gypsum. Ozkul (2000) has showed that the use of citrogypsum and desulphogypsum instead of natural gypsum in cement results in a decrease in early strength of the mortar. However, agglomeration process increased the strength at all ages, suggesting the formation of a new crystal structure after compacting [Ozkul, 2000].

Borogypsum, a waste material formed during the production of boric acid from colemanite, is another important source of chemical gypsum. Several studies were made on the possible use of borogypsum instead of natural gypsum in cement production. Borogypsum up to 10% of the cement could be used as a set retarder. However, increasing the borogypsum level in Portland cement from 5% to 20% causes a decrease in compressive strength and tensile strength [Boncukoglu et al, 2002]. Calcined borogypsum in cement application decreases soundness and markedly increases the setting time and 28-day compressive strength of the mortar compared to that of untreated borogypsum [Elbeyli et al, 2003]. But disadvantage of using wastes containing boron in cement production is their long setting time and slow early-strength development [Kula, 2001; Kula, 2002; Targan, 2003; Singh, 2002].

Phosphogypsum (PG) is a kind of gypsum that occurs as a by-product and is obtained from phosphate rock during the production of phosphoric acid. PG contains some impurities such as P_2O_5 and F cause retarding (delay) in setting time and decrease the strength of Portland cement. So in order to use it as a cement retarder instead of natural gypsum, purification, drying, and calcination processes must be applied [Erdogan, 1994; Smadi, 1999]. Mehta and Brady (1977) reported that addition of 2% SO_3 to raw mixture decreased temperature of clinkering and the retarding effect but increased early strengths. Altun and Sert (2004) found that PG that was stored in

open-air (weathered) residue areas for several years can be used in place of NG for Portland cement according to Turkish standards. The highest 28 days compressive strength was found in the sample with 3 wt% PG [Altun & Sert, 2004].

2.3.2 Waste Gypsum

Another kind of gypsum can come from the hydration of plaster of Paris and is known as waste gypsum. When gypsum ($CaSO_4.2H_2O$) is ground to a powder and heated at 150 ^{0}C to 165 ^{0}C, three quarters of its combined water is removed producing hemihydrate ($CaSO_4.0.5H_2O$), commonly know as plaster of Paris. When this powder is mixed with water, it will result in the setting of the paste as the water recombines to produce gypsum again. This kind of waste gypsum can be obtained from the ceramic factory (plaster mould), gypsum building products and plasterboard [British Geological Surver, 2006].

2.3.3 Dehydration of Gypsum

When gypsum i.e. calcium sulfates dihydrate ($CaSO_4.2H_2O$) is heated to a temperature about 150^{0}C, it will lose about three quarters of its water to form calcium sulfate hemihydrate ($CaSO_4.0.5H_2O$) and total hydration at temperatures 170^{0}C – 190^{0}C, forming soluble anhydrite ($CaSO_4$) [Papageorgiou et al, 2005]. Such temperatures can occur during the cement grinding process and result in the formation of significant quantities of $CaSO_4.0.5H_2O$ (hemihydrate) and $CaSO_4$ (anhydrite). The ratios in which these calcium sulphate forms occur in cement can have a profound effect on the setting behavior, because their respective solubilities in water are significantly different from one another. Upon mixing with water, hemihydrate and anhydrite react readily with water to form needle-shape crystals of gypsum. This leads to gypsum precipitation and some rigidity or stiffening of the concrete or mortar, making it necessary to add more water for workability and resulting in a lowering of the strength

properties. This process is referred to as “False Setting". The dihydrate form is the preferred form required in cement [Strydom & Potgieter, 1999].

The amount of dihydrate, hemihydrate and anhydrite can be determined by DSC/Tg (Figure 2.4). The first peak at 140 ^{0}C is the dehydration of dihydrate to hemihydrate (Equation 2.8), where the mass loss of this peak corresponds to the loss of 1.5 moles of H_2O. The second peak at 181 ^{0}C is the dehydration of hemihydrite to anhydrite (Equation. 2.9), where the mass loss of this peak corresponds to the loss of 0.5 moles of H_2O.

$$CaSO_4.2H_2O \longrightarrow CaSO_4.0.5H_2O + 1.5H_2O \quad \text{…….(Equation 2.8)}$$

$$CaSO_4.0.5H_2O \longrightarrow CaSO_4 + 0.5H_2O \quad \text{…….(Equation 2.9)}$$

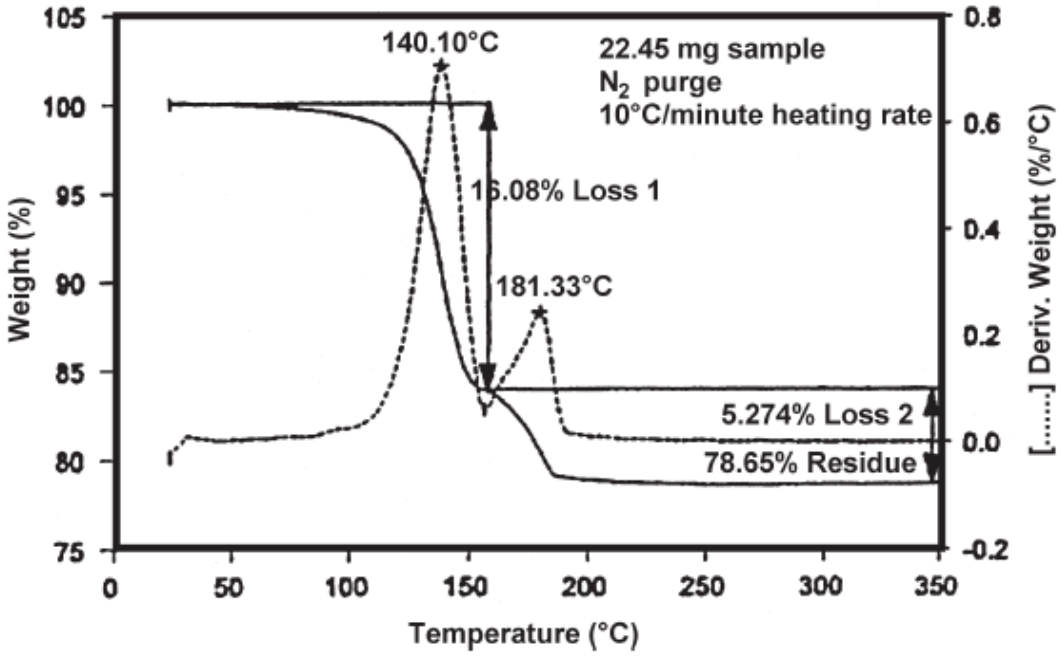

Figure 2.4: DSC/Tg of gypsum in a partially sealed container with pinhole in lid [Ramachandran et al, 2002]

The presence of a pinhole in the crucible lid increases the potential pressure sufficiently to give two separate peaks (Figure 2.5), one for the dihydrate to hemihydrate conversion and the other for the hemihydrate to anhydrite reactions. Two peaks also result when the sample bed thickness increases for the open lid condition and mass of sample containing in crucible [Ramachandran et al, 2002].

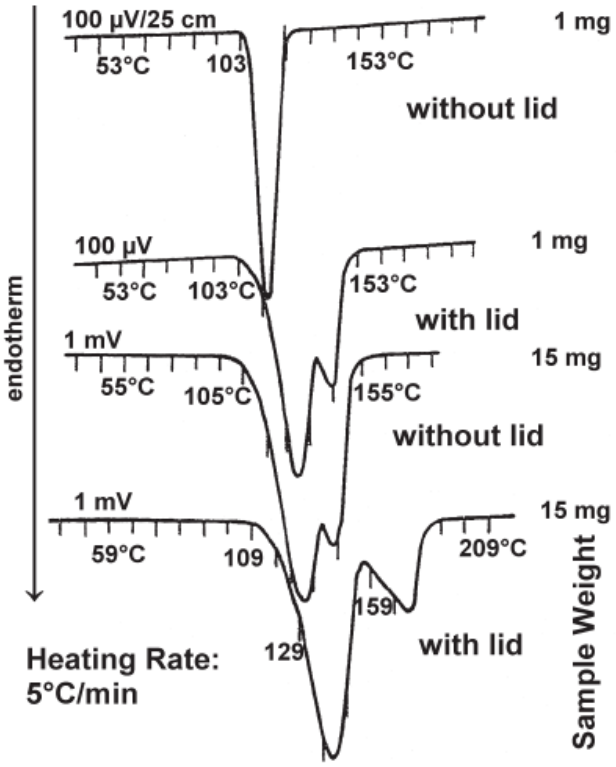

Figure 2.5: Infuence of experimental parameters on the DTA curves of gypsum [Ramachandran et al, 2002].

2.4 Grinding Clinker and Gypsum to Produce Cement

After it leaves the cooler, clinker is conveyed to a covered store. Cement is produced by grinding clinker and gypsum, usually in the ball mill (Figure 2.6). This is essentially a large rotating drum containing grinding media, normally steel ball. As the drum rotates, the motion of the balls crushes the clinker. The drum rotates approximately once every couple of seconds. The drum is generally divided into two or three chambers, with different size grinding media. As the clinker particles are ground

down, smaller media are more efficient at reducing the particle size still further. Power consumption in ball mill Portland cement is of the order of 45 kWh/t for a surface area of 360cm^2/g. This may be reduced by employing a closed circuit system, the saving of 2 – 5 kWh/t depending on the efficiency (fan powder requirement) of the separator. The principal variables to be considered in optimizing energy consumption in a ball mill include: the speed of rotation of the mill, its ball size grading and loading, and the design of its lining.

Figure 2.6: Cement mill for grinding clinker and gypsum [Understand Cement, 2002]

For years, ball mills (BM) have been the standard equipment for comminution of raw materials and cement production. But today, vertical roller mills (VRM), as shown in Figure 2.7, have become the principal choice for both raw materials and cement grinding [Ruth et al, 2000; Simmons et al, 2005]. A common characteristic of all vertical roller mills is size reduction that is affected by rollers or comparable grinding elements traveling over a circular bed of material and that material after passing under the