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CHARACTERISATION OF THE EFFECTS OF AN APPARENTLY ATYPICAL CEMENT CLINKER ON STRENGTH DEVELOPMENT OF MORTARS

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A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in partial fulfilment of the requirements for the degree of Master of Science in Engineering.

Johannesburg, 2012

DECLARATION

I declare that this research report is my own unaided work. It is being submitted for the Degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

……

(Signature of Candidate)

…….. day of ……..., ……

(day) *(month)* *(year)*

ABSTRACT

This research project presents a study that investigated the effects of a cement manufacturing process on the characteristics of the cement clinker and the resultant effects on mortar strength and heat of hydration. Two clinkers were assessed, one manufactured under unusual conditions, and the other manufactured under more normal conditions. The two cement clinkers were characterised by microscopy and x-ray diffraction in order to classify the cement clinker by their chemical composition and crystal structure characteristics. Cement was then made in the laboratory from the two clinkers. Using laboratory tests, the cements were assessed in order to determine the impact of their clinker characteristics on the engineering performance of the cement. These included; heat of hydration and mortar strength tests. The tests results showed that the manufacturing process had not affected the chemical composition of the apparently unusual clinker but had affected its crystal structure and morphology. Nevertheless, although the clinker's crystal morphology had been altered there was no significant impact of these alterations on the strength performance of the cement.

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LIST OF SYMBOLS AND ABBREVIATIONS

American Standard Test Method	ASTM
British Standard	BS
Dicalcium Silicate	C_2S
Nitiric Acid	HNO_3
Pottassium Hydroxide	KOH
South African National Standard	SANS
Tetracalcium Aluminoferrite	C_4AF
Tricalcium Aluminate	C_3A
Tricalcium Silicate	C_3S
X-ray diffraction	XRD
X-ray fluorescence	XRF

CHAPTER ONE

INTRODUCTION

1.1 Background

Concrete is amongst the most commonly used, durable and versatile materials used in construction, that has kept pace with our most modern and pressing needs (Robertson, 2002). A report published in 2007 by the United States Geographic Services showed that about 7.5 cubic kilometres of concrete are made each year. This is more than one cubic meter for every person on earth. In volume terms, this most likely makes concrete the most abundantly used man-made material in the world.

Concrete is a synthetic rock containing sand and gravel as aggregate, bonded in a cementitious matrix (Winter, 2009). The performance of concrete, mainly its strength and durability, is the sum of the individual contributions of each of the main ingredients. Cement is the key ingredient as it is considered to be the glue that binds the individual ingredients within concrete together and is responsible for its high strength (Wansborough et al, 1990). Extensive research has gone into improving concrete performance as it finds more uses in the civil engineering field. Through this research it has become apparent that a better understanding of the material is achieved by more detailed studies of the individual ingredients. Portland cement is the main contributor to the properties of concrete, thus an understanding of its characteristics will assist with improving its performance. To adequately research cement, it would be necessary to start with its manufacturing process.

1.2 Project Justification

Due to the large costs involved in cement manufacture, making variations to the energy-intensive pyroprocessing technology in a commercial production line for research purposes would be wasteful and very costly. Thus whenever an opportunity to assess an unusual cement at a large scale avails itself, it is considered valuable. Such an opportunity provides us with the possibility of better understanding the effects of cement manufacture on cement characteristics and its consequent effects on concrete performance. This research report was based on one such opportunity.

Under normal operating conditions and with reasonably consistent raw materials, a cement factory will produce clinker with fairly uniform characteristics. A Southern African cement manufacturing plant, at one particular instance, due to erratic coal and electricity supply to the plant, experienced a problem while producing clinker. This was suspected to have resulted in a clinker with characteristics suspected of being unusual to the specific plant and to Southern Africa. This clinker presented an opportunity to compare the effects of such production variations with a more conventionally produced clinker.

The main concern related to the change in the manufacturing process was the rate and extent of heating the raw materials in the kiln as well as the rate of cooling of the clinker as it emerged from the kiln. While there was no evidence as reports of unusual performance of the cement when used in concrete it was felt that the effects of these changes required further investigation.

1.3 Project Objectives

This research project attempts to assess the effects of this unusual cement manufacturing process on the characteristics of cement clinker and to determine the impact of these on mortar strength. As a basis for comparison with the apparently unusual clinker termed the reference clinker, a second clinker, manufactured under standardised conditions but at a different plant was selected. These two clinkers were crystallography characterised by microscopy and x-ray diffraction in order to classify them by their chemical composition and morphological characteristics. The two clinkers were crushed with an appropriate amount of gypsum to obtain "laboratory cements". Mortar samples were prepared with these cements and these were used to compare the strength and heat of hydration characteristics of the two cements. An attempt was then made to explain the performance of the two cements in relation to the clinker characteristics.

1.4 Project scope and limitations

In this research project, mortar strength was investigated rather than concrete strength. This is due to the cement standard (SANS 50197-1) specifying cement strength based on mortar samples. Thus, using mortar would allow the cement performance to be compared against the standard specifications for cement. Furthermore, the normal cement content in mortar ranges between 20% and 33% while in concrete it is between 14% and 16%. Thus the effects of a particular cement on strength would be amplified in mortar samples due to the higher cement content.

A limitation of the study is that the two clinkers are not entirely comparable since they are produced from different raw material sources. Thus variations in the behavior of the cements could be due to the type of raw materials utilized. The unavailability of a

standardised clinker sample from the cement plant that produced the atypical sample gives rise to this limitation. However, the reference clinker still served to give an indication of how a clinker produced under more regular conditions would behave.

When cement is mixed with water an exothermic, heat releasing, reaction occurs. The heat released during this reaction is known as the heat of hydration. The amount of heat released and the rate of its release can give an indication of the cement composition. In this research project the heat of hydration released by the two mortars was calculated using an adiabatic calorimeter. The adiabatic calorimeter tests were carried out at a constant water to cement (w/c) ratio for both mortars. The strength characterisation of the mortars was done by determining the flexural strength of mortar beams at a single w/c ratio and the compressive strength of mortar cubes at three different w/c ratios.

1.5 Report Outline

This research report is divided into chapters covering the following topics:

- A literature review of evolution of cement, factors that affect cement properties and a background on the tests done in the research.
- A detailed description of the materials used and the test methods employed
- A detailed discussion of the experimental results
- A discussion on the implications of the results and recommendations for future research

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This section presents a review of the literature on the history of cement, the factors that influence its characteristics and the methods that are used to assess its performance. It follows the progress made through continual research into cement and lays out the different methods that are used in the assessment of cement quality and how these methods have evolved over the years. It concludes with an overview of the chemistry of South African cements.

2.2 Evolution of Portland cement

Hydraulic cement, i.e. one which hardens upon mixing with water, has been utilised since Roman times. Over the years, the methods used to make cement have evolved in sophistication and level of control over quality. The pioneering cements were created from limestone and pozzolana mixed with fine brick powder. John Smeaton, in 1758 noticed that adding around 20–25% clay and heating the mixture produced cement that could harden under water. The improved cement was called hydraulic lime (Wansborough et al, 1990). In 1824, Joseph Aspdin obtained a patent for his "kitchen" manufactured cement. He heated finely ground limestone and clay on a kitchen stove and ground the mixture into a powder to create a hydraulic cement. This product was named Portland cement because of its resemblance to a stone quarried on the Isle of Portland off the British Coast. Although Aspdin's cement was of inferior quality, it laid the foundation for the modern-day Portland cement manufacturing process (Portland Cement Association, 2011). Bye (1999), reports that only two key changes have improved on Aspdin's product:

- The introduction of gypsum in order to slow the onset of setting.
- The use of higher burning temperatures in order to produce silicates with a higher lime content

Bye (1999), reports that these "*improvements were made possible by the gradual replacement of a vertical shaft kilns by the rotary kiln and the introduction of the ball mill for grinding cement"*. The rotary kiln allows the materials to move down much slower, thereby allowing the material to attain these higher temperatures. The ball mill allows thorough mixing of the clinker and the gypsum to make cement.

2.3 Manufacture of Portland cement

Modern cement is manufactured to set procedures to produce a standardised cement. In South Africa the standard cement requirements are specified in the South Africa National Standard (SANS) 50197-1 "*Cement Part 1: Composition, specifications and conformity criteria for common cements*". The properties of cement can be modified by changing its chemical composition by varying the raw materials and mix proportions before introducing them to the kiln, and/or varying the rate of cooling of the clinker (St John et al, 1998). Taylor (1997) investigated the effect of major compositional variations on cement clinker reactivity and reports that the ability of a substance to act as a hydraulic cement is dependent on two factors:

- the ability to sufficiently react with water and at a satisfactory rate
- the solid reaction products must be of very low solubility with a microstructure that yields the required physical properties, such as mechanical strength and volume stability.

In order to produce such cement, a well-controlled manufacturing process is required.

Cement manufacture consists of four distinct stages:

- quarrying
- raw material preparation
- clinkering
- cement milling

The raw material in cement manufacture is a mixture of roughly 80% limestone and 20% clay. The lime and silica are the main strength contributors in the cement. The iron from the clay and iron oxide, added with the other materials, reduces the temperature of the reaction and is responsible for the characteristic grey colour of cement. The raw materials are prepared by either a wet process or a dry process (Wansborough et al, 1990). In the dry process, proportioned dry raw materials are ground to a powder, mixed together and introduced to the kiln in a dry state. For the wet process, slurry is made by adding water to the proportioned raw materials. The grinding and blending processes are also performed with the materials in slurry form. (Portland Cement Association, 2011). The wet process requires more than double the energy than that of the dry process. The kiln used in the wet process is much longer than that used in the dry process (Winter, 2009). In Southern Africa cement is generally manufactured using the dry process method.

The finely ground raw materials are dried, introduced into the kiln, heated to allow sintering reactions to take place and then cooled. During the full temperature cycle in the kiln from heating to cooling, various chemical reactions and crystal formation take place to form the major mineral constituents of Portland cement. From the selection of raw materials to the cooling process, much care is taken, as each stage has a bearing on the crystallography and chemical composition of the clinker. The mineral constituents of Portland cement are formed at particular temperature ranges and time intervals. Thus,

temperature and time of heating (or pyroprocessing) are important parameters for the transformation of minerals in the clinker. The reactions in the kiln can be broken into a number of zones as shown in Figure 2.1.

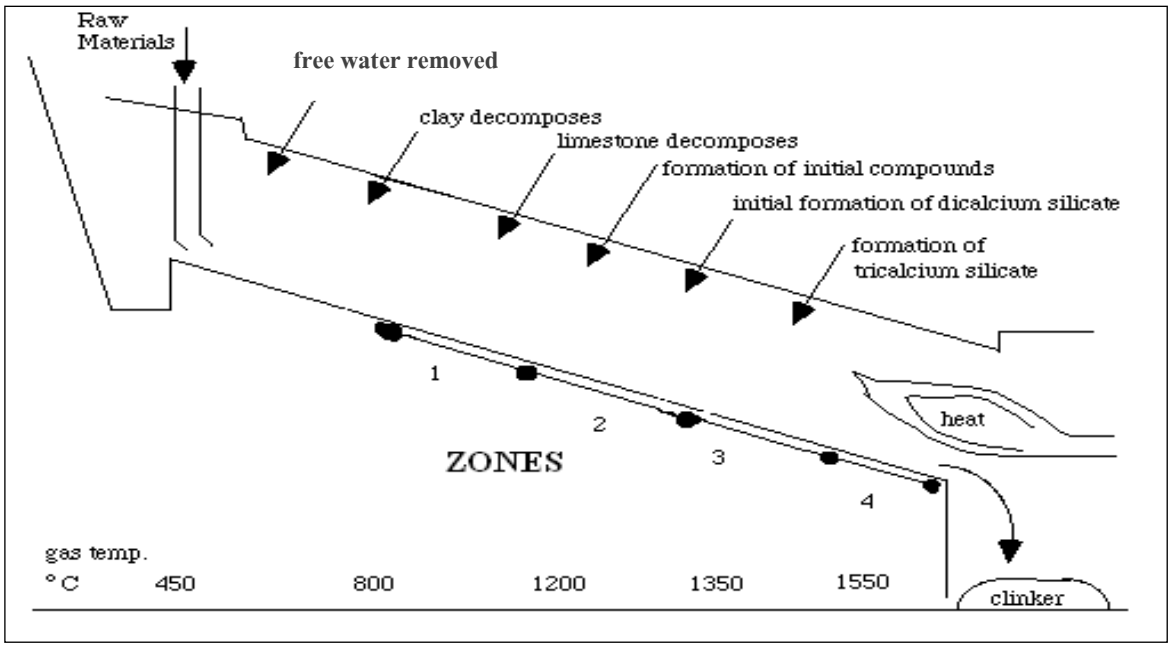


Figure 2.1: Schematic diagram of rotary kiln (after Materials Science and Technology, 1993)

When the raw meal is introduced to the kiln it moves down slowly at a controlled rate. It undergoes four fundamental stages of transformation. On entry, free water in the raw materials is removed by evaporation. Clay decomposes to aluminate and silica. Thereafter calcination occurs as the bound water and carbon dioxide is released. Clinkering is the third stage, where the calcium silicates are formed. The last stage is the cooling stage just before grinding (Materials Science and Technology, 1993). Wansborough et al (1990) breaks down the reactions that take place in the kiln into four parts and gives an approximation of the time taken in each zone.

- **<u>Zone 1: 0 - 35 min, 800 - 1100°C</u>**

  This is where the first level of reactions occurs, calcium carbonate is decomposed releasing carbon dioxide.

$$CaCO_3 \xrightarrow{heat} CaO + CO_2 \quad \text{.....2.1}$$

The formation of $3CaO{\bullet}Al_2O_3$ occurs above 900^{o}C and melting of fluxing compounds Al_2O_3 and Fe_2O_3. The fluxing compounds play an important role in the clinkering process, in that they melt at a relatively low temperature of approximately 1100˚C which allows the rate of reaction to increase significantly, accelerating the formation of the calcium silicate cement minerals.

- **<u>Zone 2: 35 - 40 min, 1100 - 1300^{o}C</u>**

  The reactions that result in secondary silicate phases occur as follows:

$$2CaO + SiO_2 \xrightarrow{heat} 2CaO{\bullet}SiO_2 \quad \text{.....2.2}$$

Above is the reaction of lime with silica and clay mineral decomposition products to give belite (an impure form of dicalcium silicate, see Table 2.1) and small amounts of ferrite and aluminate. The ferrite and aluminate that is formed at this stage may not be the same as the corresponding phases in the final clinker.

- **<u>Zone 3: 40 - 50 min, 1300 - 1450 - 1300^{o}C</u>**

  Extreme heating of raw materials to facilitate the formation of ternary silicates and tetracalcium aluminoferrates occurs.

  This is the hottest zone where the formation of the most important cement mineral occurs.

$$2CaO{\bullet}SiO_2 + CaO \xrightarrow{heat + time} 3CaO{\bullet}SiO_2 \quad \text{.....2.3}$$

$$3CaO + Al_2O_3 \xrightarrow{heat + time} 3CaO{\bullet}Al_2O_3 \quad \text{.....2.4}$$

$$3CaO{\bullet}Al_2O_3 + CaO + Fe_2O_3 \xrightarrow{heat + time} 4CaO{\bullet}Al_2O_3{\bullet}Fe_2O_3 \quad \text{.....2.5}$$

This zone is also referred to as the clinkering zone (Thomas and Hamlin, 2008). A melt is formed mainly from the refluxing agents, aluminate and ferrite, approximately

20 – 30% of the mix is liquid at 1450ºC. A large proportion of the belite and lime formed in this zone reacts in the melt to give alite (an impure form of tricalcium silicate, see Table 2.1). The material nodulizes to form clinker (Taylor, 1997).

- **Zone 4: 50 - 60 min, 1300 - 1000^{o}C**

  The various mineral phases formed in the kiln cool down and crystallise.

  This is the last stage as the clinker exits the kiln to the clinker cooler.

The clinker cooler is found immediately at the end of the rotary kiln and is designed to rapidly drop the temperature of the clinker from around 1000^{o}C to 150^{o}C. The rate of cooling is important, with more rapid cooling producing a higher $3CaO•SiO_2/2CaO•SiO_2$ ratio (see Table 2.1), thus giving a more reactive cement. It is typical to blow air or spray atomised water onto the clinker to cool it more rapidly as it exits the kiln. **(**Thomas and Hamlin, 2008**)**

The chemical reactions that take place in a rotary kiln during sintering result in the formation of the four main cement compounds shown in Table 2.1. To produce cement, the clinker is ground into a fine powder with a specific surface area of approximately 3500 cm^2/g, in vertical or horizontal roller mills. In order to regulate the rate of hydration, calcium sulphate, usually in the form of gypsum, is added during the grinding process. The amount of gypsum added depends on the chemistry of the raw materials (Bye, 1999). The addition of gypsum is meant to increase the SO_3 content in the cement. The generally acceptable SO_3 content for Southern African cements is approximately 2.3%. Natural anhydrite is introduced to discourage lumpiness of gypsum as a result of its water content. The frictional heat generated during grinding may result in the gypsum being partially dehydrated to hemihydrates, which, on further heating, dehydrates to form calcium

sulphate. The calcium sulphate is also known as a soluble anhydrite and has a higher solubility than both gypsum and the natural anhydrite. The varying proportions and solubility of the different types of calcium sulphates are important to the controlling of the cement set retardation (Winter, 2009). Because of the amount of heat generated due to friction, cement mills need to be cooled; this is accomplished by either or a combination of air and water cooling (Thomas and Hamlin, 2008).

Compound	Symbol	Chemical formula	Weight %
Tricalcium silicate	C_3S	$3CaO•SiO_2$	60-73
Dicalcium silicate	C_2S	$2CaO•SiO_2$	8-30
Tricalcium aluminate	C_3A	$3CaO•Al_2O_3$	5-12
Tetracalcium aluminoferrite	C_4AF	$4CaO•Al_2O_3•Fe_2O_3$	8-16

Table 2.1: Compound composition of South African Portland cements (Fulton, 2009)

The cement manufacturing process follows a strict production regime similar to that outlined previously in order to produce clinker of an acceptable quality, with a chemical composition as shown in Table 2.1. As extensive research on the effects of each of the steps in the manufacturing process continues, much remains unknown about the extent to which the variations in the manufacturing process affect cement quality and performance.

2.4 Factors influencing cement composition and mineralogy

2.4.1 Raw materials

Thomas and Hamlin (2008), report that although the final composition and properties of Portland cement are specified within strict bounds, the requirements for the raw mixture are not similarly strict. While it remains important to maintain correct proportions of the key compounds (calcium, silica, alumina and iron), the overall chemical composition and structure of the individual raw materials can vary considerably. This is because most

chemical components in the raw materials are burnt off and substituted by oxygen from the air at the high temperatures in the kiln. Table 2.2 lists some of the many possible raw materials that can be used to provide each of the main cement elements.

Calcium	Silica	Alumina	Iron
Limestone	Clay	Clay	Clay
Marl	Marl	Shale	Iron ore
Calcite	Sand	Fly ash	Mill scale
Aragonite	Shale	Aluminum ore refuse	Shale
Shale	Fly ash		Blast furnace dust
Sea Shells	Rice hull ash		
Cement kiln dust	Slag		

Table 2.2: Raw materials for Portland cement manufacture (after Thomas and Hamlin, 2008).

While some ingredients occur naturally like limestone and clay, others are industrial byproduct materials such as slag and fly ash. Thomas and Hamlin (2008), also highlight that not every material that contains one of the main cement elements can be used. Materials that contain certain amounts of metallic elements such as magnesium, sodium, potassium, strontium and various other heavy metals cannot be used, since these will not burn off in the kiln and will have a negative effect on the cement. Some metals like Zinc could significantly retard the early hydration process of cement (Trezza, 2007). Besides metals, other materials like quartz, which is the most readily abundant source of silica, is unreactive in its pure form even at the maximum kiln temperature and therefore cannot be used.

Clays are particularly suitable because of their fine particle size which needs little processing prior to use. They are also the most common source of silica and alumina.

Calcium is most often obtained from limestone (calcium carbonate), which is crushed and ground prior to use. According to St John et al (1998), significant amounts of 'free' lime (CaO) may occur in Portland cement clinker if the raw feed mixture is overloaded with limestone or if the mixture is not completely burned in the kiln. Excessive proportions of lime (CaO) may produce flawed cement that causes uncontrolled expansion in concrete. This leads to uneven expansion of concrete structures that may result in serviceability concerns or even compromise structural integrity of buildings.

Wansborough et al (1990), notes that the relationship between the compounds formed and the required cement performance characteristics is a chemically controlled parameter. Thus, considerable effort is made during the manufacturing of cement to ensure that the requisite chemical compounds are present in correct proportions in the raw materials before loading of the materials into the kiln. Most researchers agree that the raw material mixture is a more important parameter than the type of raw material used.

A Portland Cement Association report (2001), citing Moore (1982), reports that raw material mixture design was at the center of Portland cement quality control. The report looks at three parameters which Moore considered to be the most critical control parameters;

		Typical values	
Silica ratio	$= (SiO_2 / (Al_2O_3 + Fe_2O_3))$	2.0 – 3.0	…....**2.5**
Alumina-iron ratio	$= (Al_2O_3/FeO_3)$	1.0 – 4.0	…....**2.6**
Lime saturation factor	$= CaO / (2.8SiO_2 + 1.2\ Al_2O_3 + 0.65Fe_2O_3)$	0.92 – 0.98	…....**2.7**

The Silica ratio determines the burnability of a raw material mixture, which in turn impacts the amount of energy required by the process. As the ratio of silica to alumina and iron

increases, it becomes harder to "burn" the raw materials into the cement compounds required. As this ratio decreases, the refluxing in the reactions increases and the combining reactions become easier. The alumina to iron ratio is considered to be important because it controls the potential C_3A/C_4AF ratio in the cement as well as the cement's sulphate resistance, heat evolution and compatibility with admixtures. "*The lime saturation factor influences the C_3S/C_2S ratio in the cement. C_3S governs the early age strength development while C_2S governs the later age strength*" (Thomas and Hamlin, 2008).

Having shown the effect of each of these three control parameters on the cement quality, Moore developed a method to estimate the proportions of the four main clinker compounds (C_3S, C_2S, C_3A, C_4AF) by stating only three control parameters. For the clinker phases to be known by quantity, it is only required that the three parameters are specified for the raw materials. This showed the important link between raw materials and the cement composition.

Battagin and Maringolo (2008), also suggest that the presence of random, free lime crystals together with C_3S crystals, allied to low frequency of C_2S crystals, pointed to the use of a high Lime Saturation Factor. The authors state that, when the Silica ratio is high, silicates (C_3S and C_2S) have a high frequency while that of the clinker matrix is low. The matrix is the substance surrounding C_2S and C_3S and normally comprises of ferrite and aluminate compounds. C_3A is predominant over C_4AF when the Alumina ratio is high.

2.4.2 Pyroprocessing and cooling of cement

After careful consideration of raw materials, greater care is required to ensure the specified temperatures are attained in the kiln. Temperature and temperature duration are important

parameters for the transformation of minerals in the clinker during production. The parameters influence the formation of alite and belite during preheating and clinkering processes. The formation of belite minerals starts at a temperature near 1200^{o}C, followed by the formation of other belite polymorphs at higher temperatures (around 1300^{o}C). Finally, between 1300ºC to 1450ºC, alite minerals are formed. In general, the percentage of alite should be in the region of 60% to 70% of the crystallographic content in Portland cement in order to satisfy international standards and requirements (Mohd et al, 2007). Mohd et al (2007), showed that the chemical and mineralogical composition is affected by temperature and temperature duration. This in turn affects the clinker characteristics since clinker is normally characterised by its morphology and chemical composition.

A further aspect of temperature and temperature duration is the rate of cooling. This influences the size of crystals that are formed in the clinker. St John et al (1998), suggests that the rate at which the clinker has been cooled below 1250ºC, which is approximately the liquidus temperature, also influences the ease with which the aluminate and ferrite phases in the matrix are differentiated. Fast cooling of clinker produces more hydraulically reactive silicates and small intergrown ferrite and aluminate crystals. While slow cooling results in less hydraulically reactive silicates and coarse crystals of ferrite and aluminate. If aluminate crystals become too large they can lead to erratic cement hydration rate characteristics. Cooling the clinker very slowly allows alite to decompose to free lime and belite (Winter, 2009 and Thomas and Hamlin, 2008). It is clear from this discussion that temperature and temperature duration have a major influence on the final characteristics of a clinker.

2.4.3 Cement compounds and heat of hydration

The amount of heat generated during cement hydration and the rate at which heat is generated by the cement is strongly influenced by the mineralogical and chemical composition of the cement. Not only does it influence the heat generated but it also affects rate at which the hydration reactions occurs (Ballim and Graham, 2004). Considering the contribution made to heat development by the main compounds of Portland cement, Cannon et al, (1986), showed that C_3A had the highest individual rate of heat output per unit mass. The heat output of the individual cement compounds is provided in Table 2.3.

Compound	Heat Output [J/g]
C_3S	502
C_2S	259.4
C_3A	866.1
C_4AF	418.4

Table 2.3: Heat output of Portland cement compounds (after Cannon et al, 1986)

Using typical Portland cement compositions, the total heat evolved upon complete hydration, would be expected to be in the region of 430 J/g with C_3S making a higher contribution to the total heat of hydration as shown in Table 2.4.

Compound	Percentage contribution (%)
C_3S	63.3
C_2S	9.2
C_3A	19.9
C_4AF	7.7

Table 2.4: Heat contribution from "typical" Portland cement (Cannon et al, 1986)

2.4.4 Cement compounds and strength development

In addition to the heat of hydration, clinker composition influences the compressive strength of cement. Lawrence (1998) suggests that cement strength is higher with alite crystals of 15 μm than of 40 μm dimensions. Figure 2.2 shows the strength development of the four main cement compounds with respect to time. C_3S makes an important contribution to early age strength up to around 28 days, which is the property of Portland cement that is of primary interest to engineers.

C_2S gains strength slowly and contributes little to the concrete strength before 28 days. It however contributes to its long term strength, even more than C_3S per unit mass, provided there is sufficient water for hydration to continue. C_3A and C_4AF make relatively small contributions to the cement strength although C_3A accounts for the initial set of hydrating cement (Wansborough et al, 1990).

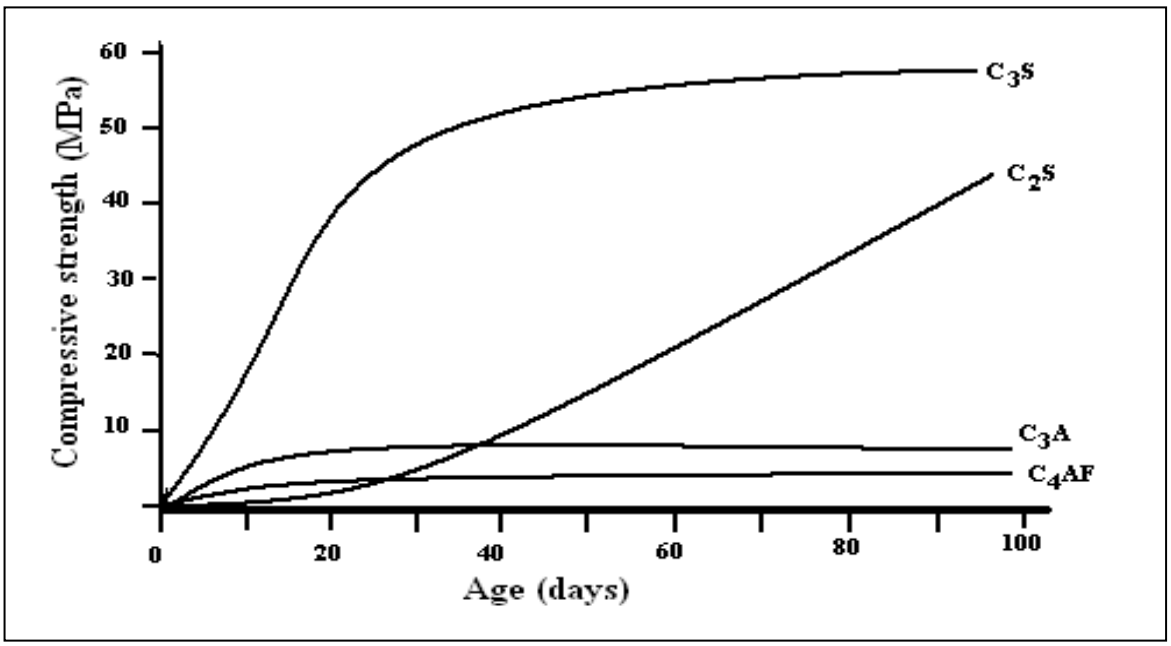


Figure 2.2: Development of compressive strength of pure compounds (adapted from Mindess et al, 2003)

2.5 Determination of cement composition

The quantitative phase composition of a crystalline material is an indispensable determinant of the relationships between its properties and the material processes that are associated with it (Roode-Gutzmer and Ballim, 2001). The strength and hydration properties of Portland cement are influenced by the presence of different compounds. However, these properties are more strongly influenced by the relative contents of the four main clinker constituents and the fineness of grinding of the cement. From the measured oxide composition of the clinker, i.e., lime, silica, alumina and ferrite, it is possible to establish the relative composition of the main clinker using the traditional Bogue approach, developed by R. H. Bogue in 1929 and modified by the American Society for Test Materials in 1996 (Bezerra et al, 2011). This ability to calculate the amounts of the major compounds in a clinker or cement made it possible to study relationships between the amounts of the compounds in cement and the engineering performance of the cement in concrete, especially in relation to durability (Frohnsdorff, 2001). Despite the usefulness of the Bogue method in explaining cement properties, it is generally agreed that the Bogue method is not sufficiently accurate in determining cement composition due to the fact that the assumptions on which the Bogue calculation is based do not prevail in practice (Bezerra et al, 2011, Bye, 1999, Glasser 1998, Taylor, 1997). One of the incorrect assumptions of the Bogue method is that the clinker is fired at 2000 ºC. Moreover, the four main clinker products are assumed to be in their pure form and there exists a fixed stoichiometric relationship between them. Since cement is not always produced under these conditions, the results obtained solving Bogue's equations often deviate from the actual composition of the clinker (Bezerra et al, 2011). The standard Bogue equations use the oxide composition of the cement to determine the potential cement composition.

$$\% C_3S = 4.071(\%CaO) - 7.60(\%SiO_2) - 6.718(\%Al_2O_3) - 1.430(\%Fe_2O_3) - 0.852(\%SO_3)$$ ……**2.8**

$$\% C_2S = 2.867(\%SiO_2) - 0.7544(\%C_3S)$$ ……**2.9**

$$\% C_3A = 2.650(\%Al_2O_3) - 1.692(\%Fe_2O_3)$$ ……**2.10**

$$\% C_4AF = 3.043(\%Fe_2O_3)$$ ……**2.11**

(after Portland Cement Association, 2011)

The inaccuracies of the original Bogue calculation led to a modification by Taylor (1997). The modified Bogue calculation appears to give better results for most modern cement clinkers or cement with an alumina ratio ranging between 1 and 4. The Modified Bogue calculation makes use of realistic compound compositions (derived from averaged micro-analytical data). Taylor's method yields four simultaneous equations which are then solved to give the potential cement composition.

$$0.710C_3S + 0.635C_2S + 0.566C_3A + 0.475C_4AF = (\%CaO)$$ ……**2.12**

$$0.252C_3S + 0.315C_2S + 0.037C_3A + 0.036C_4AF = (\%SiO_2)$$ ……**2.13**

$$0.010C_3S + 0.021C_2S + 0.313C_3A + 0.219C_4AF = (\%Al_2O_3)$$ ……**2.14**

$$0.007C_3S + 0.009C_2S + 0.051C_3A + 0.214C_4AF = (\%Fe_2O_3)$$ ……**2.15**

(after Thomas and Hamlin,2008)

Although the modified Bogue calculation is slightly more accurate than the standard Bogue calculation it has its own limitations. It is more useful when calculating cement composition rather than clinker composition. Because of the simplicity of the standard Bogue calculation it is still widely used to give an indication of the cement clinker compound composition, despite its well known inaccuracies. Glasser (1998) also concurs

by suggesting that the Bogue calculation is only meant to give a rough guide of the potential cement clinker composition not the actual composition.

Roode-Gutzmer and Ballim (2001) report that if a clinker is produced under conventional pyroprocessing conditions and the compositions of the compounds are known exactly in terms of solid solution, a fairly good estimate of the major compound composition can be attained. Methods such as reflected optical microscopy and image analysis, as well as quantitative X-ray diffraction, offer experimental tools to verify the quality of Bogue's estimates. These have proved to be effective for quantitative determination of compounds in clinkers (Bezerra et al, 2011).

2.5.1 Optical microscopy of cement clinker

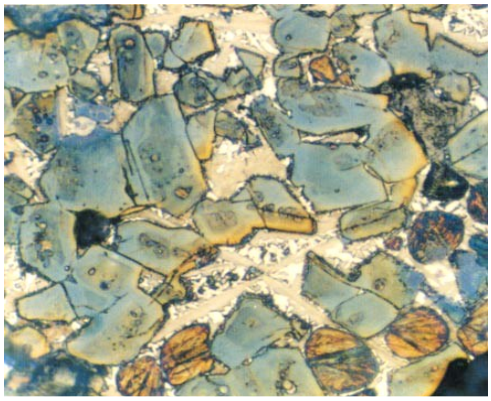
The microscopical study of Portland cement clinker commenced at the end of the nineteenth century (St John et al, 1998). In 1887 Henri Le Chateler was the first to apply the polarizing microscope to the study of cement clinkers and correctly described the crystalline compounds in cement clinkers. Ten years later, A.E. Tornebohn working without knowledge of Le Chatelier's work was able to identify four crystalline components of clinker under the microscope. The two agreed on the compound indentification but differed on the chemical composition (Graham, 2002). This rendered microscopy as more of a qualitative than quantitative tool since its results for the determination of chemical composition could not be reproduced. In 1963, Yoshio Ono applied microscopy to the determination of clinker quality and related the microstructure to strength development (Glasser, 1998). Roode-Gutzmer and Ballim (2001) consider Ono's method as a qualitative method which would be useful in assessing the clinkering process, including the raw

material preparation, burning in the kiln and the subsequent cooling. Bye (1999) also notes that microscopy is more often used to examine clinkers qualitatively than quantitatively.

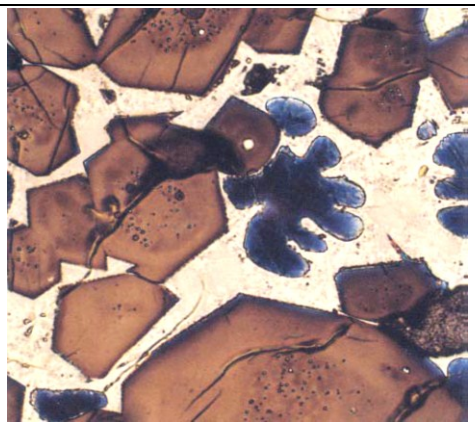
Optical microscopy has proved effective in characterizing cement clinker because much of the micro-structural detail occurs in the size range from 1μm upwards (Bye, 1999). Roode-Gutzmer and Ballim (2001) report that it is highly effective in determining adjustments to raw material composition or plant operating conditions so as to change clinker properties. Agreement exists between Taylor (1997) and Roode-Gutzmer and Ballim (2001) as the former also notes that microscopy provides information on clinker microstructure and thereby on the conditions existing at various stages of the cement manufacturing process. Campbell (1999) reports that microscopy can serve both an analytical and a quality control role in cement manufacture. He suggests that the observations from the microscopic images can be related to characteristics of raw material particles and the burning conditions in the kiln. In his discussion on optical microscopy, Glasser (1998) reports that for the determination of compound composition, optical microscopy offers certain advantages as it reveals the crystal form, abundance and spatial distribution of compounds. Figure 2.3 shows some clinker conditions that can be deduced by microscopy.

According to Glasser (1998) there are basically two methods available to determine phase abundance:

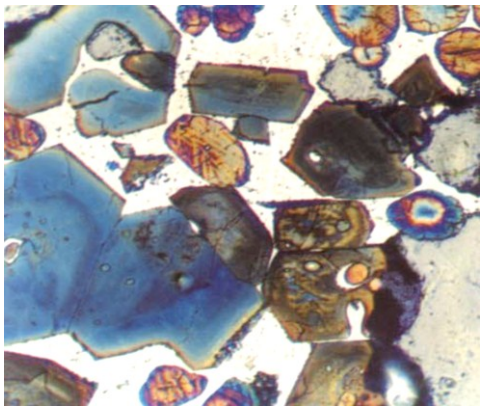
- Rosiwal-Shand method
- Glagoler-Chayes technique



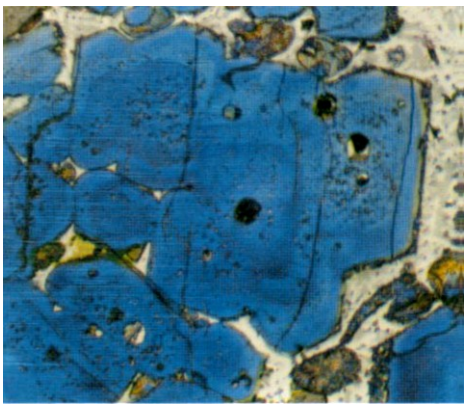
a) *Greenish blue alite crystals with thin belite coating, clinker with brown areas infers moderately low oxygen concentration*



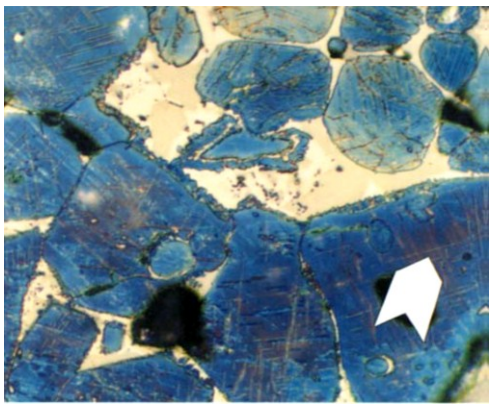
b) *Amoeboid belite crystals common in clinkers burnt at a high temperature*



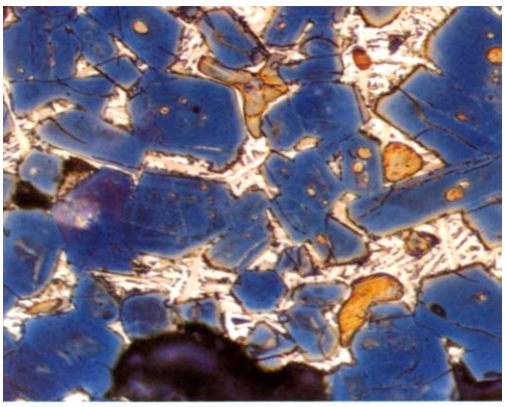
c) *Angular alite and round belite, high maximum temperature, slow heating rate, quick to moderate cooling*



d) *Euhedral alite with inclusions, small round belite and belite coating on alite infers long burning slow cooling*



f) *Alite crystals with secondary belite striations and belites fringes suggest slow cooling*



e) *Irregular brown belite wrapping around blue alite crystals typical of burning at high temperatures for a long time.*

Figure 2.3: Examples of effects of changes in manufacturing process on compound micro-structure and appearance. (Campbell, 1999)

The Rosiwal-Shand method entails the measurement of the length occupied by individual compounds along traverse lines over a thin section or a polished section. The Glagoler-Chayes technique uses a tally system to count the number of points defined by the intersection of a grid over an identified compound. According to Roode-Gutzmer and Ballim (2011), Glagoler-Chayes' technique is considered the most accurate to date. Despite the availability of methods to quantify clinker compounds using microscopy, it largely remains a qualitative tool, as research continues to find other methods to determine chemical composition of clinker. Recent research findings have identified the quantitative x-ray diffraction method as the more promising method in quantitative analysis.

2.5.2 X-ray diffraction analysis

"*X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of materials*" (Bruker, 2011). XRD offers a convenient way to determine the mineralogical analysis of crystalline solids. If a crystalline mineral is exposed to x-rays of a particular wavelength, the crystal structure diffracts the rays and produces a pattern of peak diffraction intensities, characteristic of the mineral. When the sample contains more than one mineral, the intensity of characteristic peaks from the individual minerals is proportional to their abundance. XRD can be used for both qualitative and quantitative analysis (Kumar and Monteiro, 1998). Chatterjee (2001) describes XRD as the elastic scattering of x-ray photons by atoms in a periodic lattice. The scattered monochromatic x-rays that are in phase produce constructive interference similar to those in Figure 2.4.

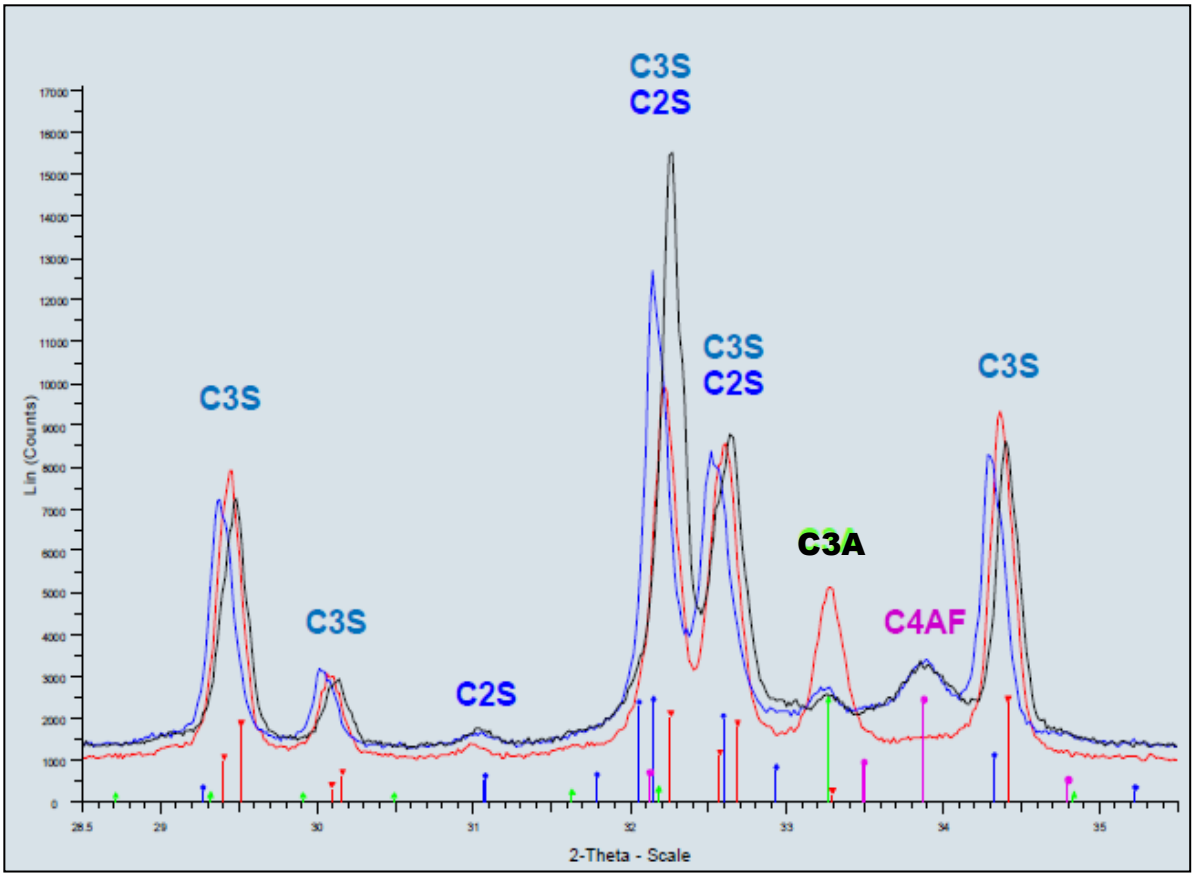


Figure 2.4: Typical XRD pattern for cement clinker (after Bruker, 2011)

Depending on the direction of incidence of the x-ray beam, in relation to the crystal lattice structure, different peak intensities occur at different diffraction angles, depending on the particular lattice spacing. The angle of diffraction (θ) follows the Bragg equation:

$$\sin\theta = \frac{n\lambda}{2d} \quad \text{.....2.16}$$

Where: λ is the wave length of the x-rays, *d* is the crystal lattice spacing and *n* is an integer. Hence, different spacings (*d*) within the same crystal will show intensities at different angles (θ) (Roode-Gutzmer and Ballim, 2001).

The major challenge with developing satisfactory quantitative XRD routines for cement arises from two issues (after Glasser, 1998):

- The dominance of alite, which overlaps the reflection peaks of other crystals in the cement
- The existence of minor polymorphic variants of the principal phases, which result in the splitting of reflections with consequential intensity changes.

In Figure 2.4 alite dominates the diffraction pattern with 5 peaks, belite with 3 and aluminoferrite peaking only once. Roode-Gutzmer and Ballim (2001), report that the quantitative XRD analysis methods applied to cement in 1982 were regarded by Aldridge as unreliable. The authors however, report that in 1984 Gutteridge managed to produce good quantitative XRD results. The general doubt about the usefulness of XRD results persisted until the advent and incorporation of the Rietveld method. This is a mathematical, multi-parameter model that utilises the full information content of the diffraction pattern (Roode-Gutzmer and Ballim, 2001). Despite its earlier shortcomings, Glasser reports that quantitative XRD has long been recognized as a tool offering great potential for the quantitative analysis of clinker crystallographic structure.

2.6 Heat of hydration

When cement and water are mixed, an exothermic chemical reaction occurs resulting in the evolution of heat termed the “heat of hydration”. As discussed in the previous sections, the heat of hydration is influenced by the chemical and mineralogical composition of a cement. Thus an accurate measurement of the heat released during cement hydration gives good indication of the chemical and mineralogical composition of the cement. The determination of the heat of hydration is particularly important in mass concrete structures because of the greater thermal gradients across the structure, as a result of differential heat

dissipation. These thermal gradients may lead to thermal cracking when the concrete heats up and later cools (Lawrence, 1999 and Graham, 2002). Figure 2.5 shows a typical heat of hydration curve. The hydration process occurs in three stages as shown in Figure 2.5 (Roy, 1989 and Muench et al, 2005). Stage 1 commences immediately upon mixing water with cement and results in high heat liberation. This is due to initial hydration of C_3A. After the initial reaction, heat rate decreases due to the formation of ettringite which retards the hydration of C_3A. This period is known as the induction or the dormant period. During this period the hydration of C_3S proceeds slowly and heat is evolved at a lower rate. The second stage involves a rapid reaction where the second hydration peak is created. This is the main period of hydration where calcium silicate hydrates (CSH) and calcium hydroxide ($Ca(OH)_2$) are formed. The reaction rate increases rapidly to a maximum and then drops again rapidly to a value which is sometimes less than half its maximum. During this stage a third peak is often encountered due to the conversion of ettringite to the monosulphate hydrate form (Winter, 2009; Graham, 2002; Muench et al, 2005). Muench et al (2005) report that at the end of the second stage 30% of the cement has hydrated and the cement has undergone both initial and final set.

The activity in this stage is mainly due to the hydration of C_3S. C_2S and C_3A do however also hydrate in this stage. Thereafter hydration continues slowly during the last stage and, according to Thomas and Hamlin (2008), the degree of hydration in this stage will depend on the w/c ratio, the cement particle size and the curing conditions. They also report that the hydration process will continue until one of the three criteria is met:

- All the cement reacts
- No water is available for hydration
- No space is available for new reaction product to form

Although there is a general agreement on the hydration process, Graham (2002) reports that there are different theories around the actual hydration mechanics. The one theory supports the "topochemical" concept, whereby reactions take place directly at the surface of the cement compounds. The other, which is the "through-the-solution" concept, involves dissolution of anhydrous compounds to their ionic constituents, the formation of hydrates in solution, leading to precipitation due to their low solubility. The current thinking is that both these concepts apply and take place simultaneously. These theories have lead to the development of different heat of hydration measurement methods.

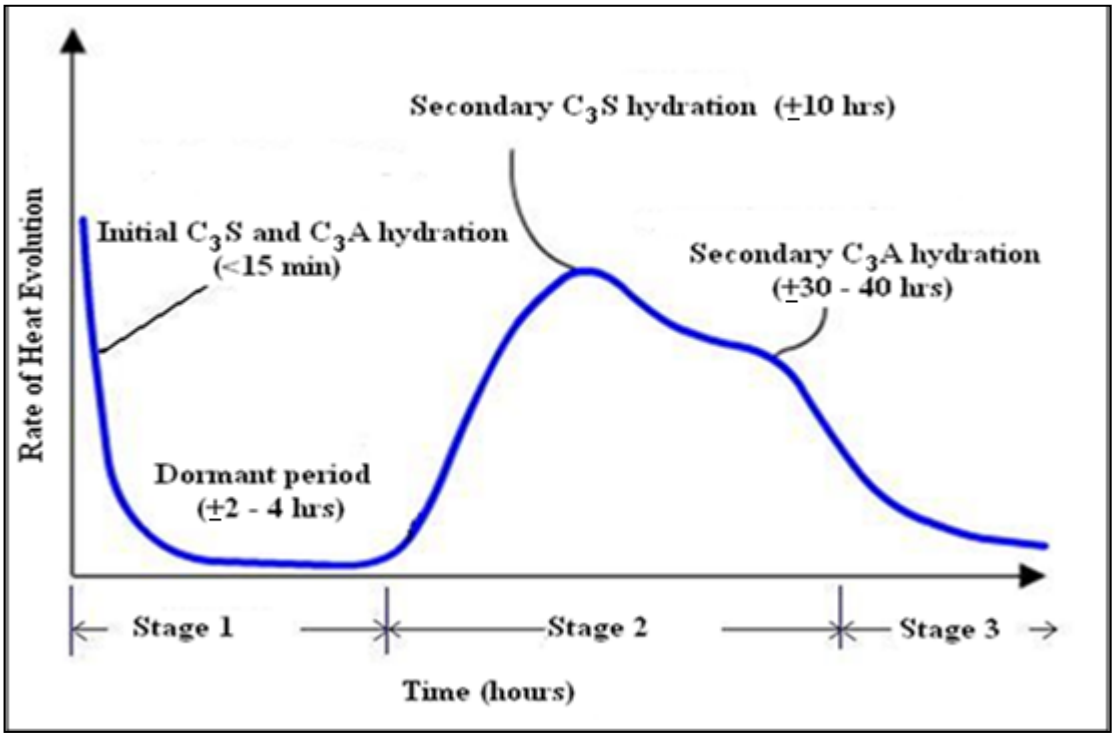


Figure 2.5: Typical heat rate curve for hydrating Portland cement (after Muench et al. 2005)

Lawrence (1998) mentions three main methods of measuring heat of hydration, namely; heat of solution, conduction and adiabatic calorimetry. He describes isothermal calorimetry as a method under conduction calorimetry while Gibbon and Ballim (1996) and Graham (2002) present the two as separate methods. Lawrence (1998) reports that the heat of

solution has become the traditional method and is even specified in various national standards (British standard (BS 4550-1978) and the American standard (ASTM C 186-82)). The method is based on the difference in the heat of dissolution of partly hydrated and unhydrated cements in a mixture of nitric acid and hydrofluoric acid. The heat differences are measured at a particular age of hydration and are an equivalent to the heat of hydration at that age (Lawrence 1998). Graham (2002) reports that the method cannot determine the rate of heat gain and that it generally provides total heat values lower than those indicated by other methods. It is therefore not conservative with respect to total heat evolved.

The conduction calorimetry method measures the heat flow from hydrating cement paste. Although the method can be used to determine heat rates it does not allow the sample to attain the temperature that would be experienced by an actual structure constructed with the particular concrete mixture (Gibbon et al, 1997).

Isothermal calorimetry measures the heat of hydration directly by monitoring the heat flow from the sample when both the sample and surrounding environment are kept at isothermal conditions (Spigelman, 1995). Gibbon et al (1997) reports that the isothermal method is similar to the adiabatic method in that it also attempts to prevent heat loss to the surrounding environment. Gibbon et al (1997) and Spigelman (1995) report that one difficulty with isothermal calorimetry and the adiabatic is capturing heat released during the initial mixing of the cement and water.

The third method is adiabatic calorimetry, the method allows for the determination of both the total heat and the rate of heat produced by a specific concrete mix. This is possible

since there is no heat loss from the test sample or gain from surrounding environment. In this method the environment surrounding the concrete sample is temperature controlled to match the sample temperature and thereby ensuring no heat transfer (Carlson and Forbrich, 1938).

Graham (2002), in his comparison of the three calorimetric methods notes that the adiabatic calorimetric method has none of the disadvantages associated with other methods. He also notes that results from this method provide input basis for temperature prediction models and an area of comparison for different concretes. And to be able to compare heats of hydration of different cements, Carlson and Forbrich (1938) suggest that the results are best expressed directly as joules per gram of cement.

2.6.1 Maturity and the heat of hydration

Since hydration of cement is a chemical reaction, it is not difficult to recognise that the rate of heat evolution in this process is related to both the time of reaction and the temperature at which the reaction takes place. The simultaneous effects of time and temperature on the evolution of the properties of hardening concrete is referred to as maturity. In his comparison of various maturity functions, Naik (1985) concluded that the Arrhenius function gave a much better maturity versus strength relationship than other maturity functions over a wide range of concrete curing temperatures. He also recommended that the Arrhenius function be used when the concrete is cured at low temperatures. Graham reports that the functions have mainly been used in connection with determining the compressive strengths of concretes exposed to different time-temperature regimes. Ballim and Graham (2004) and Lawrence (1998) make use of the form of Arrhenius equation given below.

$$K = A\ exp\left(\frac{-E}{RT}\right) \quad \textbf{2.17}$$

Where:

K is the specific hydration rate constant (energy/mole)

E is the activation energy for hydration

R is the universal gas constant

T is the absolute temperature

A is a constant

The same equation (after Naik, 1985) expressed as a maturity function, $f(T)$:

$$f(T) = k\ \exp\left(\frac{-E}{RT_k}\right) \quad \textbf{2.18}$$

Where:

k is the proportionality constant

T_k is the temperature of the concrete (in degrees Kelvin)

E is the activation energy (in joules per mole)

R is the universal gas constant

Ballim and Graham (2004) propose that the "*rate of heat evolution determined from an adiabatic calorimeter test should be normalised with respect to maturity rather than time*." They also state that the heat rate curve can be normalised such that it is independent of the starting temperature in the adiabatic test. This is achieved by expressing the maturity heat rate as a function of cumulative maturity. In order to do this, the adiabatic heat of hydration and the rate of heat of hydration are expressed in terms of equivalent maturity time (t_{20}), which is the duration of hydration if the temperature had been kept at 20ºC. The equivalent maturity time (t_{20}) is given by equation 2.12 (after Ballim and Graham, 2004) below derived from the Arrhenius equation:

$$t_{20} = \sum_{i=1}^{i=n} exp\left[\left(\frac{E}{R}\right)\left(\frac{1}{293} - \frac{1}{273+0.5(T_i+T_{i-1})}\right)\right].(t_i - t_{i-1}) \quad \textbf{2.19}$$

Where:

t_{20} is the equivalent maturity time (in hours)

E is the activation energy parameter (33.5 kJ/mol)

R is the universal gas constant (8.314 J/ mol ^{o}C)

T_i is the temperature (^{o}C) at the end of the ith time interval, t_i

Also, the starting temperature of an adiabatic test has a large influence on both the magnitude and the time distribution of heat rate, thus the normalization. Because of the advantages associated with using adiabatic calorimetry and the convenience of using maturity time as highlighted in this review, the adiabatic results in this research report are expressed in maturity time.

2.7 Cement and mortar strength

The strength of cement is the sum of the strengths of the individual contributing compounds (Wansborough et al, 1990). Research has shown that there exists a relationship between mortar strength and both the chemical composition and clinker morphology of the cement (Thomas and Hamlin, 2008; Maki et al, 1993). The relationship between strength and these two parameters has provided a way of predicting the mechanical performance of cement during and after its hydration (Battigin and Maringolo, 2008). It is generally agreed that rapidly cooled clinker during the production process produces smaller crystals which are more reactive (St John et al, 1998 and Winter, 2009). The rapidly cooled clinker would produce a concrete that would develop strength faster than clinker which was cooled much slower. However, over an extended duration the clinkers would produce concrete of similar strength although one would attain its strength earlier than the other.

On the other hand, Lawrence (1998) reports that there are differing views on the type of relationship that exists between alite crystal size and cement strength. The author reports that although most researchers suggest an increase in strength with decrease in alite crystal size, Butt and Timashev in 1965 reported an increase in strength performance with increasing alite crystal size. While Suzukawa et al in 1964 had noted no change in strength performance due alite crystal size. The author also reports that the overall clinker grain structure may also affect cement strength performance, relating higher strength performance to relatively large, well developed crystals with well defined boundaries.

According to Svinning et al (2010), clinker strength increases most with increasing C_3S proportions and less with C_2S proportions. The author also notes that since only two silicates exist in clinker, i.e. C_3S and C_2S, an increase in one led to a decrease in the other. This meant that as the effect of the one diminishes, owing to percentage composition, the effect of the other increased. Although C_3S is key in the early strength development of cement, an excessive amount can negatively affect cement strength. Odler (1991) reports that when C_3S content is in excess of 70% cement strength begins to decline. Stanek and Sulovsky (2002) report that alite, the principal hydraulic compound of clinker, can exist in seven structural modifications i.e. three triclinic, three monoclinic and one trigonal modification. In their study they note that the modification is established during the cooling process. They also report that some modifications showed up to 10% greater compressive strength than others, implying that the modifications also changed the hydration characteristics of the cement compound. The authors also noted that SO_3 and MgO contents had a significant influence on the nature of the modification. With a decrease in

the MgO/SO_3 ratio resulting in a modification that increases the compressive strength of the cement.

Frigione and Sersale (1985), report that a certain alkali oxide content in cement clinker retarded setting of cement but in most cases did not affect the mortar strength in any way. However in the case of alkali sulphates, they note that the hydration of C_3A and C_3S is not affected while compressive strength is significantly lowered. Knofel (1979), reports that amounts of up to 1.6% of either Na_2O or K_2O in cement resulted in a decrease in both early and late strength. These studies have resulted in great care being taken to ensure that correct raw material selection and proper pyroprocessing are done in the manufacture of cement.

2.8 Variation of South African cements

Although the cement manufacturing process follows a reasonably consistent procedure, the cement produced in different factories will show some variation for reasons ranging from raw material type, kiln conditions and cooling rate. Graham (2002) assessed the range and extent of variation of heat of evolution for South African cements designated as Portland cement (CEM1) in SANS 50197-1 strength grade 42,5N. Clinker and cement from nine cement factories around South Africa and was characterized in terms of chemical composition and cement compound morphology using X-ray fluorescence (XRF), XRD and microscopy techniques. XRF is a technique that uses x-rays to provide details of the chemical composition of a sample while XRD uses the same to determine the presence and amounts of compounds in a sample. Despite the clinker and cement having been produced to meet the same specification, Graham reports significant variations in the clinker and cements. The microscopy study reports similar crystal sizes for alite and belite crystals between the 9 different clinkers.

Compounds	Compound Composition (%)
C_3S	61 – 75
C_2S	6 – 18
C_3A	3 – 11
C_4AF	5 - 13

Table 2.5: Bogue phase composition ranges for South African cements (after Graham, 2002)

Determinant	% Range
CaO	68.40 – 65.06
SiO_2	23.00 – 21.20
Fe_2O_3	1.57 – 4.26
Al_2O_3	3.80 – 5.00
MgO	1.10 – 3.70
TiO_2	0.18 – 0.45
Mn_2O_3	0.05 – 0.99
P_2O_5	0.00 – 0.16
K_2O	0.13 – 0.62
Na_2O	0.00 – 0.37

Table 2.6: Cement Oxide composition ranges for South African cements (after Graham, 2002)

The crystal size ranges noted by Graham (2002) were within those suggested by Campbell (1999) as acceptable for clinker produced under normal conditions. Table 2.5 and Table 2.6 show the calculated Bogue composition ranges and the range of variations that Graham noted for chemical analysis respectively. Graham could not account for the variations in the cements since they had all been produced under normal operating conditions. However, he concludes that since the variations were not large, any possible negative effects on strength could be minimised by appropriate concrete mixture design. The compound

composition ranges shown in Table 2.5 are nearly the same as those shown in Table 2.1, although there is a marked decline in C_2S proportions.

In order to evaluate the heat of hydration of the 9 different cement samples, Graham made use of an adiabatic calorimeter described in section 2.6 of this research report. Figure 2.6 shows the heat rate plots calculated from adiabatic calorimetry. Despite these cements having been manufactured to the same specification, they varied in the rate at which they evolved heat during hydration. The calorimeter test results showed a variation in the heat rates that allowed the cements to be placed into three categories based on their heat rates: low, medium and high heat rate cements. Graham concluded that with the exception of one clinker, there was no clearly identified relationship between clinker morphology and thermal behavior.

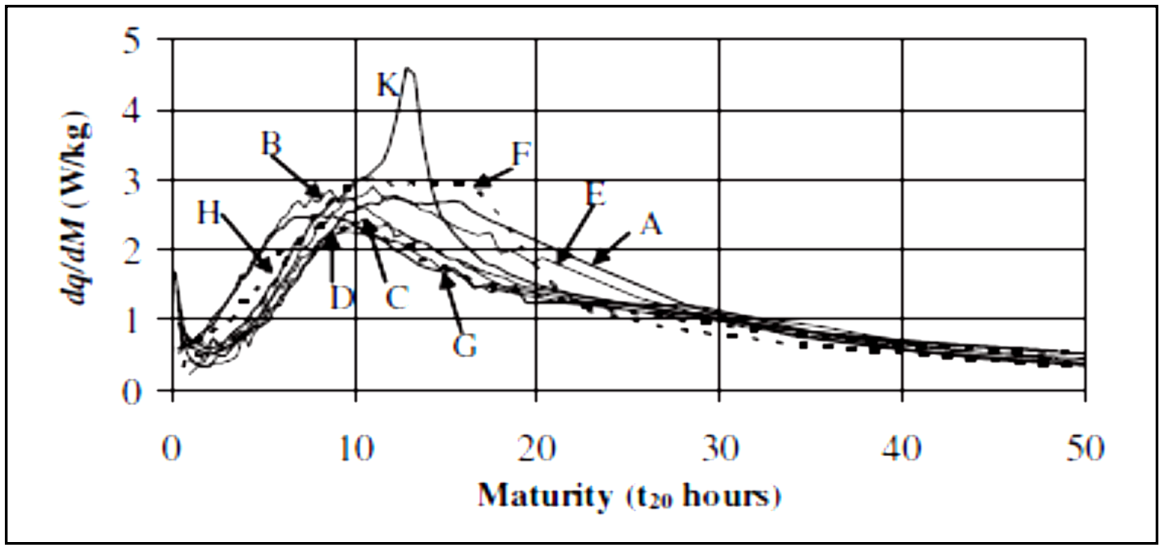


Figure 2.6: Heat rate curves for South African cements obtained using an adiabatic calorimeter (after Graham, 2004)

This showed that cements produced at different factories under normal operating conditions were bound to vary in characteristics. Hence cement specifications are not specified as definitive figures but rather ranges which set the required limits.

2.8 Closure

The objective of this research report was to assess the effects of an unusual cement manufacturing process on the characteristics of cement clinker and its resultant effects on mortar strength. Guided by the review in this section, in order to answer the research question, the chemical composition, XRD, microscopy and strength of the cement clinker were assessed. The following chapter provides details of these assessments.

CHAPTER THREE

MATERIALS AND METHODOLOGY

3.1 Introduction

This chapter provides details of the procedures that were followed in undertaking this investigation as well as the materials used. Firstly, it deals with the sampling and properties of the materials that were used for testing. Details are presented on how the clinker was collected, how the cement was made and how they were both stored before they were used for the various tests. Secondly, a description of all the tests carried out in this investigation is presented, with details of the sample preparation and testing procedures for each test. The samples were prepared to ensure that both cements had been treated in the same way so that, on testing, any variations in performance would mainly be a result of the differences in clinker characteristics. This was important since the aim was to have a reliable basis for the comparison between the apparently atypical clinker and the conventional clinker.

3.2 Materials

3.2.1 Cement clinker sample collection

Cement clinker samples were collected from two manufacturing plants owned by the same company: one where the clinker had been produced under 'unusual' pyroprocessing conditions (Clinker A) and the other clinker, produced under standardised conditions, but at a different plant (Clinker B). This second clinker was used as a reference clinker against which to compare the characteristics of the first clinker. Clinker A was collected at the grinding mill and Clinker B was taken from the cement plant laboratory. Approximately 4kg of each clinker was used in the test programme. Of this amount, about 500g was kept

for microscopy and chemical analysis. The remaining clinker material was then used to prepare laboratory-cements using a small scale grinding mill. The cement samples were kept free from moisture by sealing them in labelled plastic bags which in turn were placed in labelled plastic buckets with an air-tight lid.



Figure 3.1: Physical appearance of Clinker A as collected

3.2.2 Cement sample manufacture

To manufacture the cement samples, a single sample of gypsum was obtained from one of the cement plants. The oxide composition results for the gypsum and the clinkers determined by x-ray fluorescence (discussed later) were used to calculate required amount of gypsum to be added to the clinker to obtain an SO_3 content of 2.3 % of the cement. The use of the same gypsum type and SO_3 content was important to ensure that the results from the heat of hydration and strength tests of the two clinkers were compared on the basis of clinker characteristics only.

The two cement samples were milled at the laboratory of one of the cement plants. The two clinkers, with the calculated and measured amounts of gypsum, were ground to the same fineness typical of a 42.5 N (**N**ormal setting) cement type (3500 ± 50cm^2/g). The specific surface area of the sample was determined using the Blaine test. The measured properties

of the cements, as determined in the laboratory are shown in Table 3.1. The amount of gypsum added to Cement A was approximately half that added to Cement B, clearly illustrating the differences in the raw material properties used to make the two cements.

	Cement A	Cement B
Natural Gypsum added (g/kg of clinker)	28.6	50.1
Relative Density	3.13	3.09
Specific Surface Area (cm^2/g)	3550	3500

Table 3.1: Clinker A and Clinker B characteristics determined in the laboratory

3.3 Test methods

The tests conducted on Clinker A and Clinker B are grouped into two categories as shown in Table 3.2.

Aspect	Test methods
Clinker and cement characteristics	X-ray fluorescence
	X-ray diffraction
	Optical microscopy
Performance of cement	Adiabatic calorimetry
	Mortar strength test

Table 3.2: Test methods categories

These test methods are described in more detail in the sections which follow.

3.3.1 X-ray fluorescence (XRF)

An X-ray fluorescence method was used to determine the oxide composition of the cements. The analysis was conducted in the laboratory of the cement plant where the

cement samples were prepared. A Bruker S8 Tiger x-ray spectrometer was used for this analysis. This XRF facility is used for regular quality control purposes at the plant. The main oxides detected in both cements are indicated in Table 4.2 in chapter 4.

3.3.2 X-ray diffraction (XRD)

The compounds present in the clinkers were identified by X-ray diffraction analysis. The XRD analysis was conducted at the same laboratory where the XRF tests were undertaken. The samples were prepared and analysed in the same manner used at the plant to analyse cement samples during routine quality control testing. The analysis was done using a Bruker D8 Advance x-ray diffractometer. The XRD traces for the two clinkers are shown in Figure 4.5 and Figure 4.6 in chapter 4.

3.3.3 Optical microscopy

The crystal structure of the clinkers was investigated by optical microscopy at the Civil Engineering laboratory of the University of the Witwatersrand. The microscopy unit comprises an optical microscope, as shown in Figure 3.2, a digital camera and a desktop computer with an image analysis facility. The microscope is a Nikon eclipse polarizing microscope, which allows both transmitted and reflected light for sample examination. The head of the microscope provides for binocular viewing with a monocular tube which allows for digital imaging connections like cameras and projection devices. The microscope provides magnifications of 50X, 100X, 200X and 400X. To view and analyse the clinkers under the microscope, the samples were prepared in the manner described by Graham (2002) and is briefly explained below.

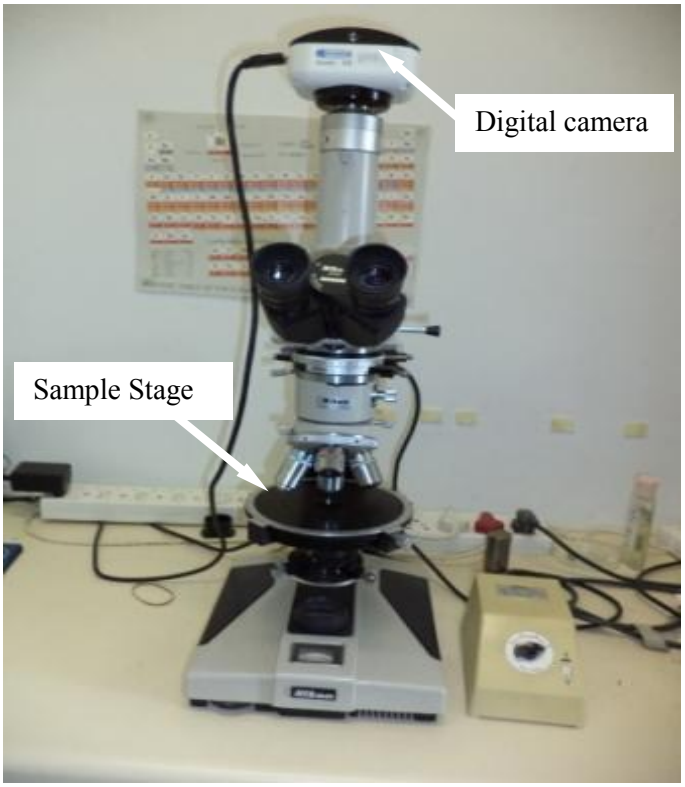


Figure 3.2: Optical Microscope

Clinker preparation Approximately 250 grams of each clinker sample was lightly crushed using a steel pestle. The material was sieved and the fraction of the material passing through a 2.36 mm sieve and retained on a 1.18 mm sieve was used for encapsulation and mounting.

Encapsulation and mounting The clinker fragments obtained after sieving were used to prepare three 30 mm diameter polished specimens. The specimens were prepared as follows:

- Clinker particles were loosely placed in the bottom of the polished sample moulds (see Figure 3.3) to approximately a third of the mould height
- A low viscosity epoxy was mixed and poured into the moulds until it completely covered the clinker fragments. The epoxy and the clinker were thoroughly mixed to eliminate any visible entrapped air.

- The moulds were then placed in a desicator for 20 minutes at a vacuum pressure of 75 kPa to further remove any remaining air.
- The moulds were then filled with epoxy
- The moulds were returned to the desicator for further 15 minutes with the same applied vacuum pressure.
- The moulds were then allowed to stand until the epoxy had hardened.





Figure 3.3: Moulds for the preparation of the polished sections

Grinding and polishing After the epoxy had hardened, the specimens were ground and polished as follows:

- The clinker face of the samples was held against a rotating sander to ensure a flat surface and remove any surface pits.
- The samples were then manually rubbed on a grade P400 sandpaper placed on a glass plate until the surface was completely flat. A straight edge was used to check the flatness of the samples.
- When suitably flat, the prepared surfaces were observed under a binocular microscope, at low magnification to check for any larger or deep scratches. Rubbing of the sample on the P400 sandpaper continued until no scratches were observed under the microscope, only then was the polishing process started.

For the polishing process the samples were then placed in a Struer's Rotopol 31 Lapping Machine equipped with a Struer's Rotoforce 4 mounting arm that enables six samples to be polished simultaneously. The polishing process is described below:

- A disc with a 6 µm diamond paste (DP) pan cloth was installed in the machine and cleaned with a paper towel and alcohol.
- A small amount of 6 µm DP suspension was placed on the pan and was spread across the surface of the disk using the ground face of the sample.
- The samples were then mounted in the Rotoforce arm and rotated for 6 minutes at a downwards force of 15 Newtons.
- After 6 minutes the samples were removed from the machine and cleaned with isopropyl alcohol in an ultrasonic bath.

The cleaned specimens were observed under a low-magnification binocular microscope for scratches. If any scratches were apparent the steps set out above were repeated until the sample was scratch-free.

The samples that were deemed to be free of scratches went through the same process described above but using the parameters shown in Table 3.3.

DP pan cloth size (µm)	Downward force (N)	Rotation time (min)
3	10	4
1	5	5

Table 3.3: Parameters used for 2nd and 3rd polishing cycles

Etching In order to be able to distinguish between the constituent compounds of the clinkers under a microscope, it is necessary to etch the clinker surfaces that had been polished in the manner described above. The procedure followed for etching was as described by Graham (2002) and involved the following steps:

- Four petri dishes were set out in a row (Figure 3.4(a))

- The first dish was filled with a 1% solution of KOH and ethyl alcohol; the second with ethyl alcohol; the third with a solution made up of 1.5 ml HNO_3 and 100ml of isopropyl alcohol (nital) and the fourth with isopropyl alcohol.
- The polished face of the sample to be etched was dipped into the first dish, containing the KOH solution for 20 seconds (Figure 3.4(b)). At the end of this period it was immediately transferred to the second dish to be rinsed and stop the reaction.
- The sample was then briefly dipped in the fourth dish and buffed lightly with a paper towel.
- Finally the specimen was dipped in the third dish for 6 seconds and then transferred immediately to the fourth dish for rinsing.



a) Petri dishes laid out b) Immersing samples

Figure 3.4: Etching of samples for microscopy test

The etched specimens were then stored in an air tight container with silica gel crystals for later viewing under the microscope. Figure 3.5 shows the finished polished sections on silica gel ready for viewing under the microscope.



Figure 3.5: Polished specimens on a bed of silica gel crystals

3.3.4 Heat of hydration measurement

The heat of hydration of the cement was measured using a low cost adiabatic calorimeter developed by Gibbon et al (1997) at the University of the Witwatersrand laboratory. A schematic arrangement of the calorimeter is shown in Figure 3.6. The calorimeter requires a 1 litre concrete sample. The concrete sample is placed in a sample chamber which allows for a 40 mm thick air space between the concrete sample and sample chamber. This keeps the concrete from being in direct contact with the water since the air gap induces a temperature lag which is necessary to dampen any harmonic responses because of the inherent error in the two temperature probes. One temperature probe, to monitor the concrete temperature, is inserted into the center of the concrete sample while a second temperature probe is placed in the water tank. The water temperature is automatically controlled via a desktop computer with an installed analogue-digital input/output (I/O) card installed on it. The analogue-digital I/O card enables the desktop computer to switch the heater element in the water tank on or off in order to ensure that the water temperature is at the same level as that of the concrete. The temperature of the concrete is then monitored

over time and the amount of heat released per unit mass of cement is then determined (Graham and Ballim, 2004).

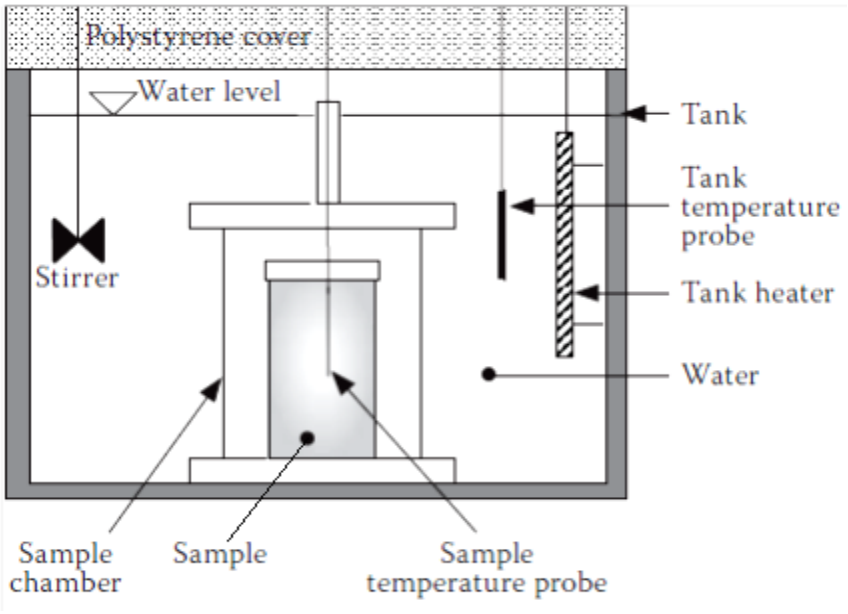


Figure 3.6: Adiabatic calorimeter (after Graham et al, 2011)

Sample preparation The calorimeter tests were conducted using the same mixture proportions used to prepare the concrete test samples. These mixture proportions are shown in Table 3.4.

Material	Quantity (g)
Cement	420
13mm Silica stone	1020
Silica sand	1060
Water	280

Table 3.4: Concrete Mixture Proportions for Heat of Hydration Tests

The procedure for preparing the concrete sample and initiating the test is given:

- A mixing bowl was placed on a scale accurate to ± 0.1 g and the reading was zeroed. The required amount of silica stone and silica sand was then weighed in the bowl.
- The scale was zeroed and the cement was measured into the same mixing bowl, together with the aggregates.
- The mixing bowl was removed from the scale and a 1 litre plastic sample container was placed on the scale, after zeroing the scale, the required amount of water was poured in to an accuracy of 0.1 g using a measuring cylinder and a pipette.

After measuring out the materials, the dry mixture was blended manually until the whole mixture appeared uniformly grey in colour. The temperature of the mixture was monitored to ensure that it was within 2ºC of that of the water in the tank temperature. If the temperature was too high, the dry mixture was covered and placed in a freezer to bring down the temperature, if too low the mixture was briefly placed in 50ºC oven to raise the temperature. After obtaining the required temperatures the test proceeded as follows:

- The water in the plastic container, which had been left standing in the room for 24 hours to equilibrate to room temperature, was added to the dry mixture and mixed
- The mixture was mixed manually until it had uniform consistency
- The concrete was then transferred to the plastic container incrementally compacting the concrete by lightly and regularly tapping the container on the table with every layer placed in the container. The consistency of the concrete mixture allowed good compaction to be obtained in this manner.
- The container was filled below the rim. Figure 3.7 shows a filled sample container ready to be placed into the calorimeter.
- The mass of the concrete sample was measured to an accuracy of 0.1 g and recorded



Figure 3.7: Concrete sample in the plastic container

Sample testing After weighing the sample it was quickly placed at the center of the sample chamber and the temperature probe was then pushed into the center of the concrete sample as shown in Figure 3.8a. The sample chamber was then closed and lowered into the water bath within 10 minutes of adding the water to the solid materials for mixing. The assembled sample chamber in the water tank is as shown in Figure 3.8b. The polystyrene tank cover was then put in place and the test was allowed to run until the temperature change in the concrete had reduced to less than 0.5 ºC in a 24 hour period.

During the test the concrete temperature was monitored and the amount of heat per unit mass of cement (q_t) was determined from:

$$q_t = C_p.(T_t - T_0).\frac{m_s}{m_c} \quad \text{.....3.1}$$

Where:

C_p is the specific heat capacity of the concrete, determined as the mass weighted average of the specific heat capacities of the concrete components, (1115.8 J/kg.K);

T_t is the temperature of the concrete sample at time *t* during the adiabatic test (K) and;

T_0 is the sample temperature at the beginning of the test (K);

m_s is the mass of the concrete test sample (kg);

m_c is the mass of cementitious binder in the concrete sample (kg).

In order to normalize the calculated heat results for variations in temperature during adiabatic test, the results are analysed and presented in terms of maturity (t_{20}) rather than time, using the Arrhenius function (Ballim and Graham (2004)):

$$t_{20} = \sum_{i=1}^{i=n} exp\left[\left(\frac{E}{R}\right)\left(\frac{1}{293} - \frac{1}{273+0.5(T_i+T_{i-1})}\right)\right].(t_i - t_{i-1}) \quad \textbf{3.2}$$

where:

t_{20} is the maturity time (in hours) at an equivalent temperature of 20ºC

E is the activation energy parameter (33.5 kJ/mol)

R is the universal gas constant (8.314 J/ mol ^oC)

T_i is the temperature (^oC) at the end of the i^{th} time interval, t_i



a) Concrete sample in the sample chamber



b) Sealed sample chamber in the water tank (Tank cover removed)

Figure 3.8: Adiabatic Calorimeter

3.3.5 Cement mortar strength

The cement mortar strength tests were carried out in accordance with the specifications ASTM C109 (2002), for compressive strength and the BS EN 196-1(2005), for flexural strength. The mortar sample details and test schedule are shown in Table 3.5 below.

Test type	Sample Size (mm)	Test Ages (days)	w/c ratios	No. of Samples per mix
Flexural strength	40 x 40 x 160	3,7,28	0.5	9
Compressive strength	50 x 50 x 50	3,7,28	0.3; 0.4; 0.5	9

Table 3.5: Mortar Strength Test Schedule

Mortar composition The flexural strength was assessed using a single w/c ratio while the compressive strength was assessed using mortars with three w/c ratios; 0.3, 0.4 and 0.5. A sand-cement ratio of one part cement to 2.75 parts graded silica sand as specified in ASTM C109 (2002) was used for the compressive strength test samples. A one part cement to three parts graded silica sand as per BS EN 196-1 (2005) specification was used for the flexural strength test samples. The proportions of the mortar mixtures are given in Table 3.6.

	Compressive strength mix			Flexural strength mix
w/c ratio	0.3	0.4	0.5	0.5
Water / g	150	200	250	225 ± 1
Sand / g	1375			1350 ± 1
Cement / g	500			450 ± 1

Table 3.6: Mortar mixture composition

Specimen Mould Preparation The moulds were cleaned and assembled. A thin coating of mould release oil was applied to the interior surfaces of the moulds and base plate.

Mortar Mixing Procedure The mortar was mixed mechanically using a HOBART mortar mixer. The mortar was mixed in batches as follows:

- Water was poured into the bowl and the cement was added
- The mixer was started immediately at the low speed, and allowed to run for 30 ± 1s before adding sand over a period of 30 ± 1s.
- The mixer was stopped and switched to high speed. The mixing continued for a further 30 ± 1s.
- The mixer was stopped again for 90 ± 1s. In the first 15 ± 1s of stopping the mixer mortar adhering to the sides was scraped off. The bowl was then covered for the remainder of the time to prevent loss of moisture.
- The mixture was then mixed at high speed for an additional 1 minute before casting.

Moulding Test Samples The moulding started within 2 minutes and 30 seconds after the completion of the mixing of the mortar.

Flexural Test Samples The casting of the mortar samples was done using 40 x 40 x 160 mm prism moulds. The prism moulds, were filled with mortar and hand-held on a mechanical vibrating table for 10 seconds in order to release entrapped air. Mortar was added to fill the mould, and then held on the vibrating table for a further 10 seconds. The excess mortar was struck off using a steel trowel. The surface was then smoothed using the same trowel and the samples were labeled.

Compressive Test Samples The mortar samples were cast using 50 x 50 mm cube mould compartments. Sufficient mortar was placed into the moulds to half fill the compartments.

The mortar was then compacted by tamping 32 times using a 50mm diameter in each mould compartment. The procedure was repeated until each of 50 x 50 mm compartments was full. The mortar was then made to flush with the top of the mould by scrapping the excess off using a steel trowel.

Curing Test Samples After casting, the moulded samples were covered with a plastic sheet and left for 24 hours. After 24 hours the hardened mortar samples were demoulded and submerged in water at a temperature of 22 ± 1 ºC until the required testing age.

Testing the Samples The cured test samples were removed from the curing tank and kept under a damp cloth, until they were tested. The Tinius Olsen compression testing machine with a load capacity of 600kN was used for all tests.

Flexural Strength Test (BS EN 196-1:2005) The 40 x 40 x 160 mm prism was placed in the loading machine as shown schematically in Figure 3.9 with the floated surface vertical. A load was then applied vertically (F_f) by means of the loading roller to the opposite side face of the prism at a rate of 50 ± 10 N/s until fracture. Measure from the time of mixing the strength tests were performed within the following time limits:

- 72 hrs ± 45 min
- 7 days ± 2 hrs
- 28 days ± 8 hrs

The flexural strength (R_f) was calculated from:

$$R_f = \frac{1.5 \times F_f \times l}{b^3} \qquad \text{……3.3}$$

Where:

R_f is the flexural strength;

b is the side length of the square section of the prism;

F_f is the load applied to the middle of the prism at fracture;

l is the distance between the supports.

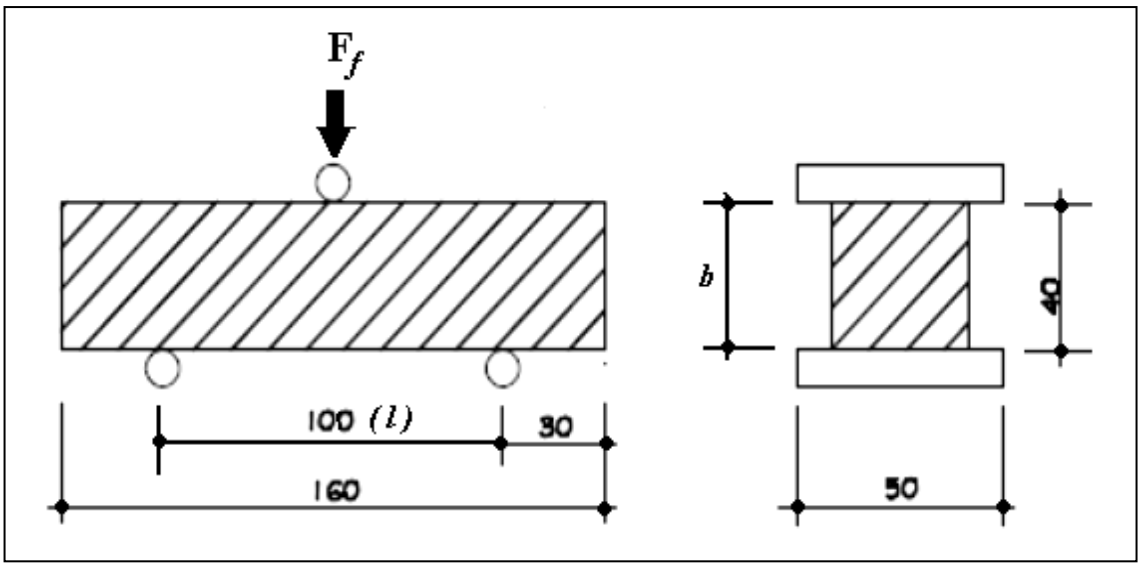


Figure 3.9: Flexural test loading arrangement

Compressive Strength Test (ASTM C109) The mortar cube was placed in the testing machine below the center of the upper bearing block as shown in Figure 3.10. The load was applied to the formed faces of the sample i.e. with the floated face vertical. The sample was loaded at a rate of 1000 N/s. Upon failure the maximum applied load was recorded and the compressive strength was calculated using equation below:

$$f_m = \frac{P}{A} \qquad \text{.....3.4}$$

Where:

f_m is the compressive strength;

P is the load at failure;

A is the area of loaded surface.



a) Sample ready to be tested in machine



b) Failed Sample after testing in the machine

Figure 3.10: Compression strength test

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

This section presents the results, analysis and discussions of the various tests conducted during the research. The results presented in this section are those for clinker microscopy, XRF, XRD, strength tests and heat of hydration test. In further analysis, the heat of hydration test results were used in a finite difference temperature prediction model to assess the likely effects of the two cements on temperature development in actual concrete structures. The finite difference temperature prediction model used in this study was developed by Ballim (2004) to predict temperature at different times and locations in large concrete elements. The model uses adiabatic calorimeter results as input to assess the impact of different clinkers in mass concrete elements. "*The model is a 2 dimensional solution of the Fourier equation for heat flow in solid bodies and is run on Ms Excel® spreadsheet*"(Ballim, 2004).

4.2 Cement clinker test results

4.2.1 Microscopy

Clinker microscopy was carried out as described in the previous chapter. In this section micrographs taken at a magnification of 400x are shown for Clinker A and B.

4.2.1.1 Clinker A

Figures 4.1 and 4.2 show micrographs of Clinker A taken at a magnification of 400x. The micrographs revealed a fairly heterogeneous clinker, containing a mixture of belite and alite crystals. The observed shapes of alite crystals were angular euhedral and subhedral with a few pseudo hexagonal crystals present. Cracks and inclusions could be seen in most

of the alite crystals. In most cases the alite crystals were joined together to form larger crystals. This is besides the fact that the individual crystals were fairly large. The sizes of the individual crystals ranged between 21.8 µm to 124.2 µm, with an average of 56.4 µm. This is well above the normal crystal size range noted by Campbell (1999), who considers the normal crystal range to be between 25 µm and 65 µm. This increase in the alite crystal sizes can be attributed to slow cooling of the clinker during production (Winter, 2009).

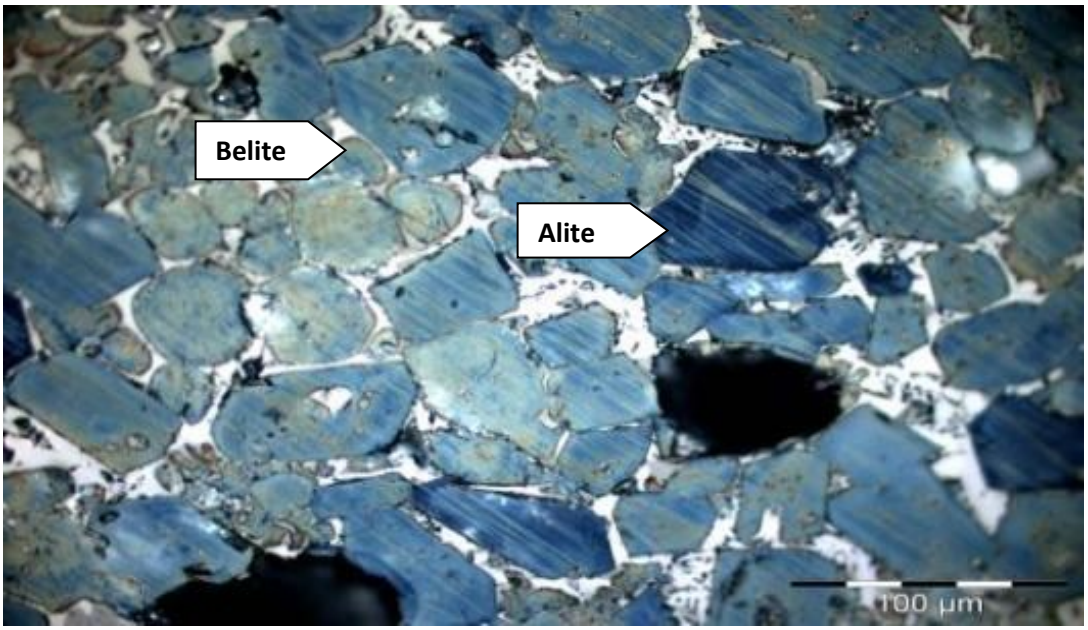


Figure 4.1: Clinker A micrograph showing alite and belite crystals

The belite particles were observed to be well rounded crystals. During microscopy very small rounded belite particles could also be seen around the edges of alite crystals. This, according to St John et al (1998), could also be attributed to slow cooling rate. The belite particle sizes ranged between 7.2 µm and 74.2 µm, with an average of 20.9 µm.

The matrix was observed to be rich in aluminate and ferrite although not always easily distinguished. It was a predominantly coarse matrix of aluminate and grey ferrite.

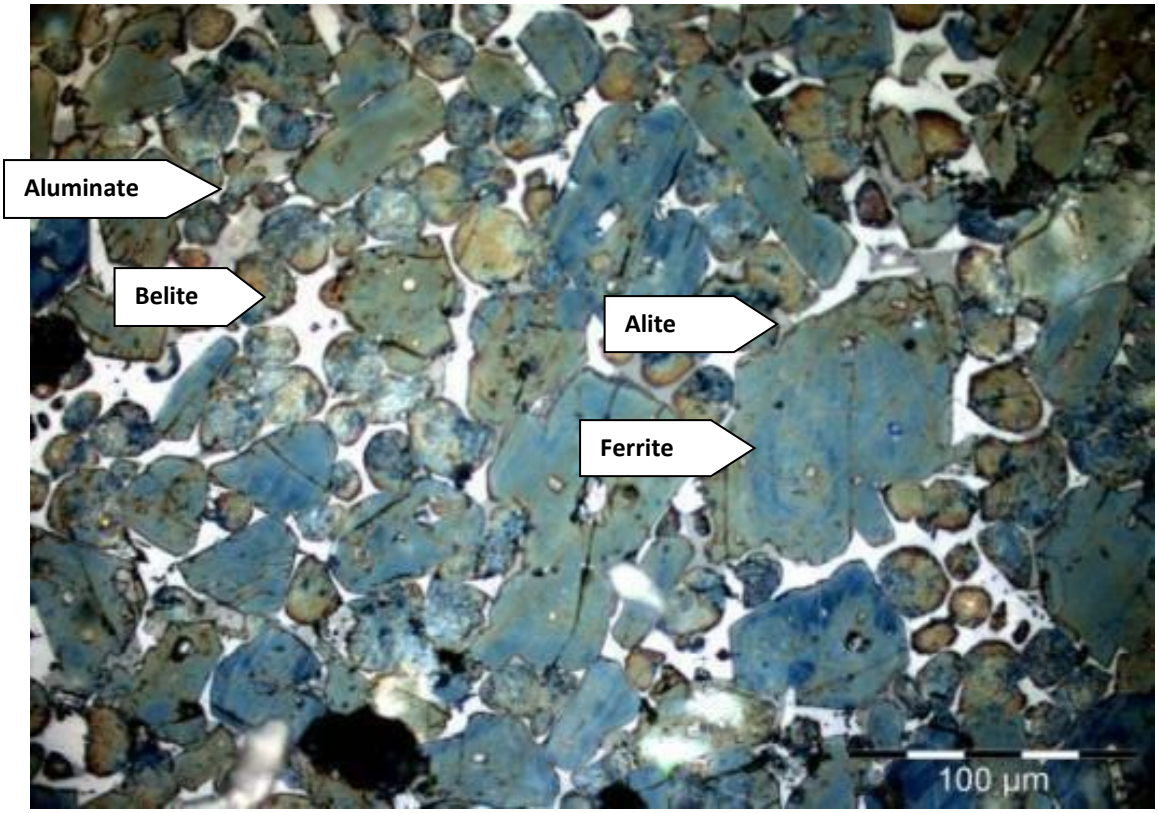


Figure 4.2: Clinker A micrograph showing microcracks in alite

Clinker A had an unusual morphology compared to more commonly encountered clinker morphology. The alite crystals were large, irregular in shape and had a number of inclusions. There was a relatively high belite presence, with complete dominance in some instances (belite nesting). The matrix appeared to be very coarse with brightly reflective ferrite and dark grey aluminate. These observations suggested that the clinker was manufactured under poorly controlled, fluctuating temperature conditions. The manufacturing process may have also experienced irregular raw meal feeds into the kiln and/or poor grinding of the raw materials which led to the nesting of belite crystals. Due to the reported erratic coal and electricity supplies, the clinker might have cooled more slowly as the rate of exit from the kiln reduced, leading to formation of large alite crystals and the decomposition of some alite to belite.

4.2.1.2 Clinker B

Figures 4.3 and 4.4 show Clinker B micrographs taken at a magnification of 400x. The microscopy revealed a high percentage of alite crystals. The alite crystals observed were hexagonal and angular euhedral in shape. A small percentage of the alite crystals were joined to one another. The crystal sizes were observed to be smaller than those in Clinker A. The individual alite crystals ranged in size between 8.8 μm and 80.9 μm with an average of 37.3 μm. This range does not differ significantly from the expected clinker size range suggested by Campbell et al (1999).

The limited number of belite crystals observed were either rounded or amoeboidal in shape. In some micrographs, belite was either absent or of negligible percentage as seen in Figure 4.4. This was supported by both the XRD results and the Bogue calculation that showed that belite proportion are normally almost six times less than alite proportions. The size of the individual belite particles ranged between 5.1 μm and 55.9 μm, with an average of 22.1 μm

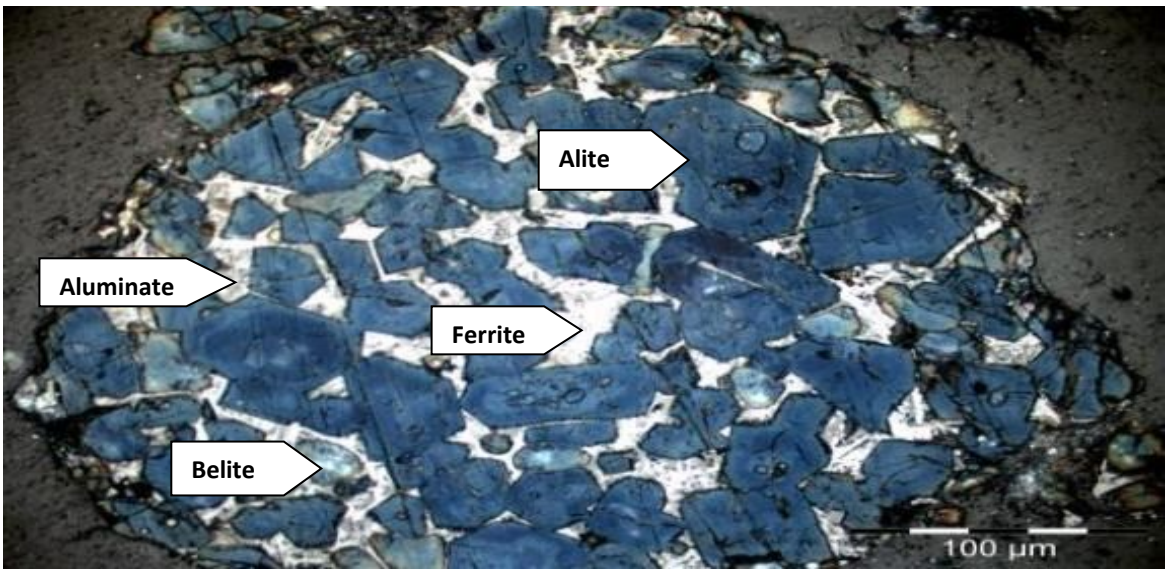


Figure 4.3: Clinker B mocrigraph showing alite, belite and a matrix of ferrite and aluminate

The matrix was observed to be a well differentiated grey aluminate and dull reflecting ferrite. Ferrite dominated the matrix with aluminate hardly visible in most cases.

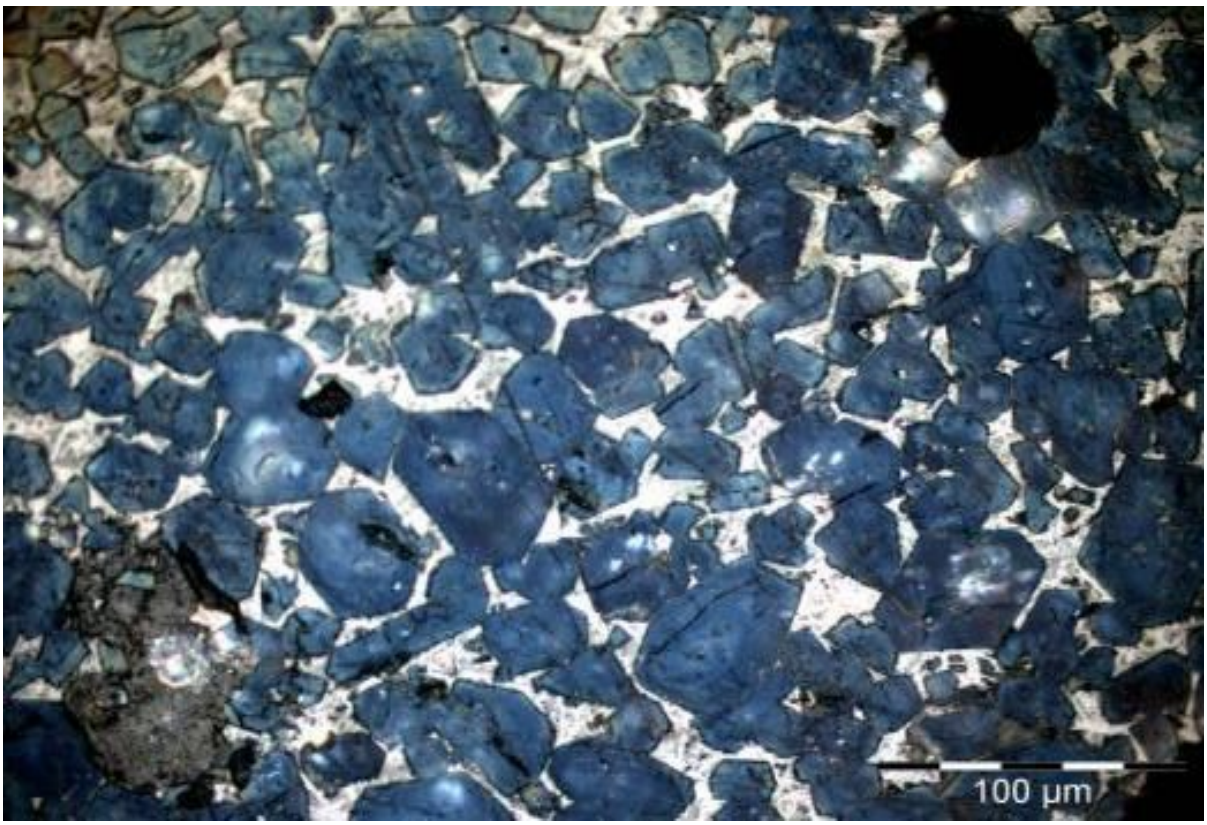


Figure 4.4: Clinker B micrograph showing mainly alite crystals

The microscopy of Clinker B revealed a clinker with commonly observed characteristics. The alite crystals where within the range specified for a standard clinker. The microscopy suggested that the clinker had been burnt at a suitably high temperature and had been cooled at a rate which allowed stable alite growth (Campbell et al, 1999).

4.2.1.3 Summary of clinker morphology

Table 4.1 shows the principal characteristics of the two clinkers.

	Clinker A	Clinker B
Alite	Angular euhedral and subhedral, pseudo hexagonal crystals. Cracks and inclusions common, size range 21.8 µm to 124.2 µm. Average size of 56.4 µm. Typical of slowly cooled clinker.	Hexagonal and angular euhedral, size range 8.8 µm and 80.9 µm. Average size of 37.3 µm. Typical of optimally cooled clinker.
Belite	Rounded and very small rounded belite particles around the edges of alite crystals, size range 7.2 µm and 74.2 µm. Average size of 20.9 µm. Typical of slowly cooled clinker.	Sparse distribution, rounded and a few amoeboidal shaped, size range 5.1 µm and 55.9 µm. Average size 22.1 µm. Typical of clinker burnt at very high temperature.
Interstitial phase	Rich in aluminate; ferrite not always easily distinguished. Coarsely crystalline matrix of grey aluminate and ferrite.	Well differentiated grey aluminate and dull reflecting ferrite.

Table 4.1: Summary of clinker morphology observations

4.2.1.4 Comparative discussion and conclusions

The microscopy revealed some significant differences between the two clinkers. The differences were more evident in alite crystals. The differences observed were as follows:

i) *Alite crystal sizes*: Clinker A crystal sizes were larger than those of Clinker B. Most Clinker A crystals were joined to form bigger crystals. According to Taylor (1997) and Winter (2009), crystal size varies inversely with cooling rate; as the cooling rate decreases the particle sizes become bigger.

ii) *Inclusions in alite crystals*: Clinker A alite crystals had more pronounced inclusions than Clinker B. According to Campbell (1999), large amounts of entrapped interstitial crystals are indicative of unstable alite growth. The conditions did not allow for uninterrupted crystal growth. This could be a result of uncontrolled temperature variations.

iii) *Microcracks in alite crystals*: Clinker A alite crystals had more micro cracks than Clinker B; this can be attributed to a rapid crystallization of the matrix (Maki, 1994). It could also be a result of the presence of iron oxide, which promotes the formation of microcracks for easy grindability (Odigure, 1999). Since the manufacturing process was interrupted, the effects of the iron oxide might have been amplified in the case of the atypical clinker.

iv) *Irregular alite crystal shapes*: Most of the alite crystals in Clinker A had irregular shapes while those for Clinker B had more of the expected hexagonal shape. The irregular shapes are also attributed to unstable alite growth (Campbell, 1999).

v) *The presence of belite crystals*: Clinker A had a higher concentration of belite crystals than Clinker B. Slow cooling might be the reason for the presence of more belite crystals in the clinker, as reported by Winter (2009) and Thomas and Hamlin (2008), since it allows alite to decompose to belite and free lime.

vi) *Belite nests:* Clinker A had some cases of belite nesting which were not encountered in Clinker B. Nesting is normally associated with irregular feeding of raw materials into the kiln and/or incomplete grinding of the raw materials (Campbell, 1999). The irregularities may have been a result of erratic electricity supply to the plant.

The differences in the morphology of Clinker A and B suggest that there was a problem in the manufacture of Clinker A. Such as they were, these unknown problems resulted in the

production of a clinker with an atypical morphology. The observed differences were expected to result in a reduction of cement strength, particularly at early ages. This is because most of the anomalies observed were related to the form and presence of alite, which is primarily responsible for early strength development in cement. This is discussed further in section 4.4.

4.3 Cement chemical composition test results

4.3.1 X-ray fluorescence (XRF)

The main oxides detected in both cements are indicated in Table 4.2. The XRF tests showed that for both the cements the oxide compositions were within the recommended ranges in South African standard (SANS 50197-1) and compare favorably with XRF produced by Graham (2002).

Determinant %	Cement A (%)	Cement B (%)	SANS 50197-1	Graham (2002) range
CaO	62.3	63.6	-	65.1 - 68.4
SiO_2	20.9	20.9	-	23.0 – 21.2
Fe_2O_3	3.02	2.88	-	1.57 – 4.26
Al_2O_3	4.07	4.36	-	3.8 – 5.0
MgO	4.49	2.69	5.0	1.1 – 3.7
TiO_2	0.23	0.28	-	0.18 - 45
Mn_2O_3	0.54	0.61	-	0.05 – 0.99
P_2O_5	0.02	0.02	-	0.00 – 0.16
SO_3	2.34	2.22	4.5	-
K_2O	0.35	0.55	-	0.13 – 0.62
Na_2O	0.40	0.40	-	0.00 – 0.37
LOI	1.33	1.56	-	-
Total	**100.1**	**99.9**		

Table 4.2: Cement oxide composition

The cause of the differences between the measured oxides contents could not be ascertained because the raw materials used in the manufacture of the clinker at each plant could not be analysed. Clinker A shows a significantly higher MgO content than Clinker B, while Clinker B shows a higher K_2O content than Clinker A. For all the other oxides, the two clinkers show relatively similar compositions. According to the British Geological Survey (1995), major variations in cement oxide composition of MgO and K_2O are possibly as a result of the use of a limestone with a high level of these two oxides.

The main cement compounds were determined by the modified Bogue calculations using the measured oxide composition from the XRF analysis and are shown in Table 4.3 below.

Compound	Cement A	Cement B
C_3S	68.5	68.9
C_2S	9.5	9.1
C_3A	2.0	3.9
C_4AF	10.9	9.9

Table 4.3: Compound composition for the two cements

The standard Bogue calculation showed that Cement B had a higher C_3S content but a lower C_2S content than Cement A. The modified Bogue calculation gave mineral compositions that corresponded with the XRD trace (Figure 4.5 and 4.6) in as far as showing that the two cements had similar mineral composition. The calculated compound composition for both cements lay within the limits specified in SANS 50197-1 for South African cements for the modified Bogue method.

4.3.2 X-ray diffraction (XRD)

The XRD trace for the two clinkers is shown in Figure 4.5 and Figure 4.6. The XRD results confirmed the presence of the following compounds in addition to other expected compounds:

- Tricalcium silicate (C_3S - Alite)
- Larnite, beta polymorph of belite (St John et al, 1998)
- Brownmillerite, a mineral of varying composition with values close to C_4AF (Graham, 2002)
- Lime
- Periclase (MgO)

The XRD trace for Clinker A shown in Figure 4.5 shows the highest peak for C_3S at about 32º 2θ, the height of the C_2S peak is 14.6% that of C_3S and occurs at 31º 2θ and C_4AF has a peak 43% of C_3S at about 34º 2θ. Figure 4.6 shows a XRD trace for Clinker B. C_3S has its highest peak at 32º 2θ while C_2S's highest peak is about 10% that of C_3S at 46º 2θ. C_4AF has a peak that 34% that of C_3S at about 34º 2θ. In both cases C_3S had the greatest number of peak occurrences while C_2S has the lower peak heights. Periclase was identified in both clinkers and the peak occurs at the same 2 theta value for both clinkers, 43º 2θ. The XRD trace for the two clinkers shows that the two clinkers have the same mineralogy, the traces are almost identical with some minerals having peaks at the same point. From the XRD trace it is not possible to distinguish between the reference clinker and the atypical clinker

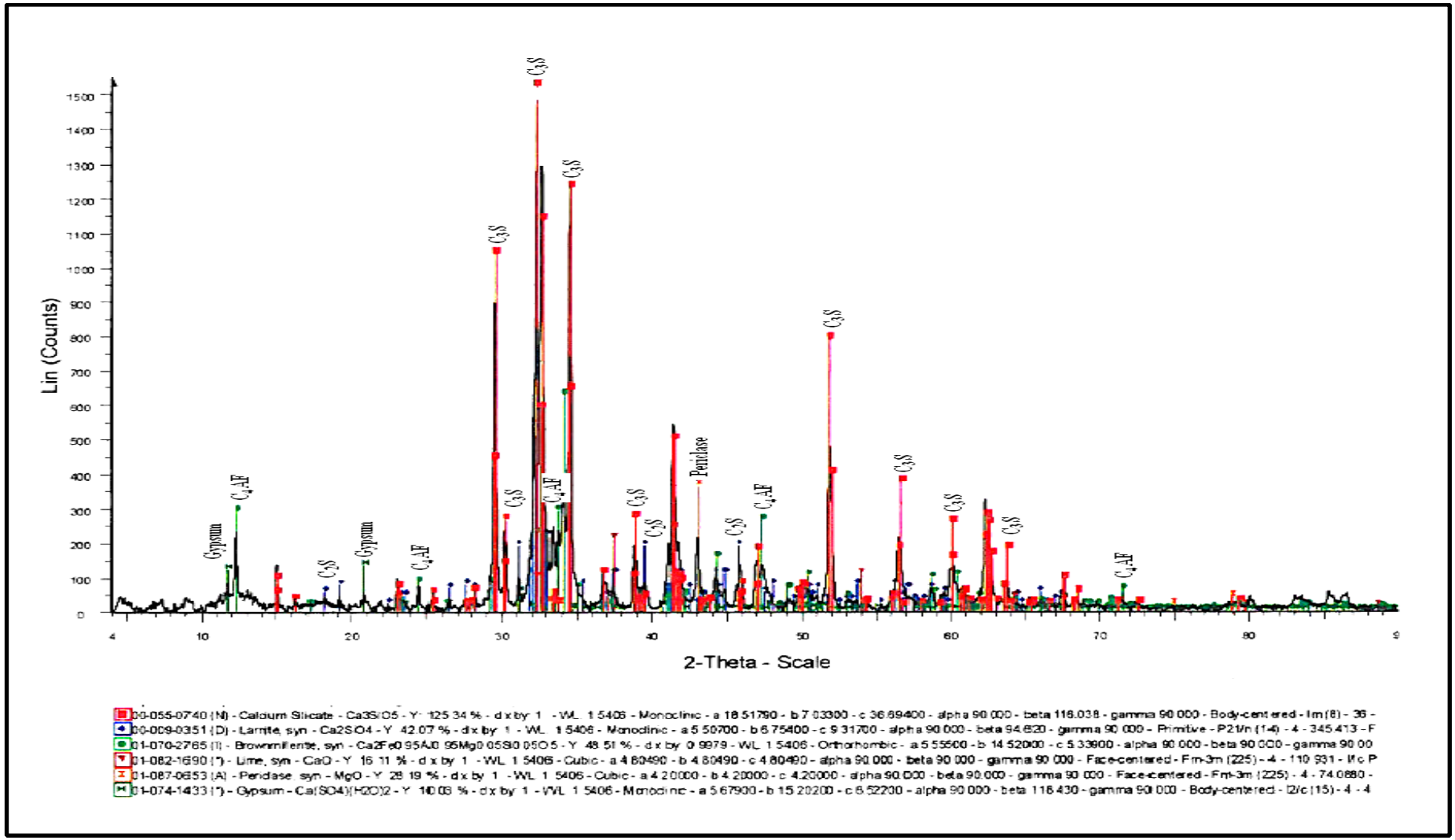


Figure 4.5: XRD trace for Clinker A cement

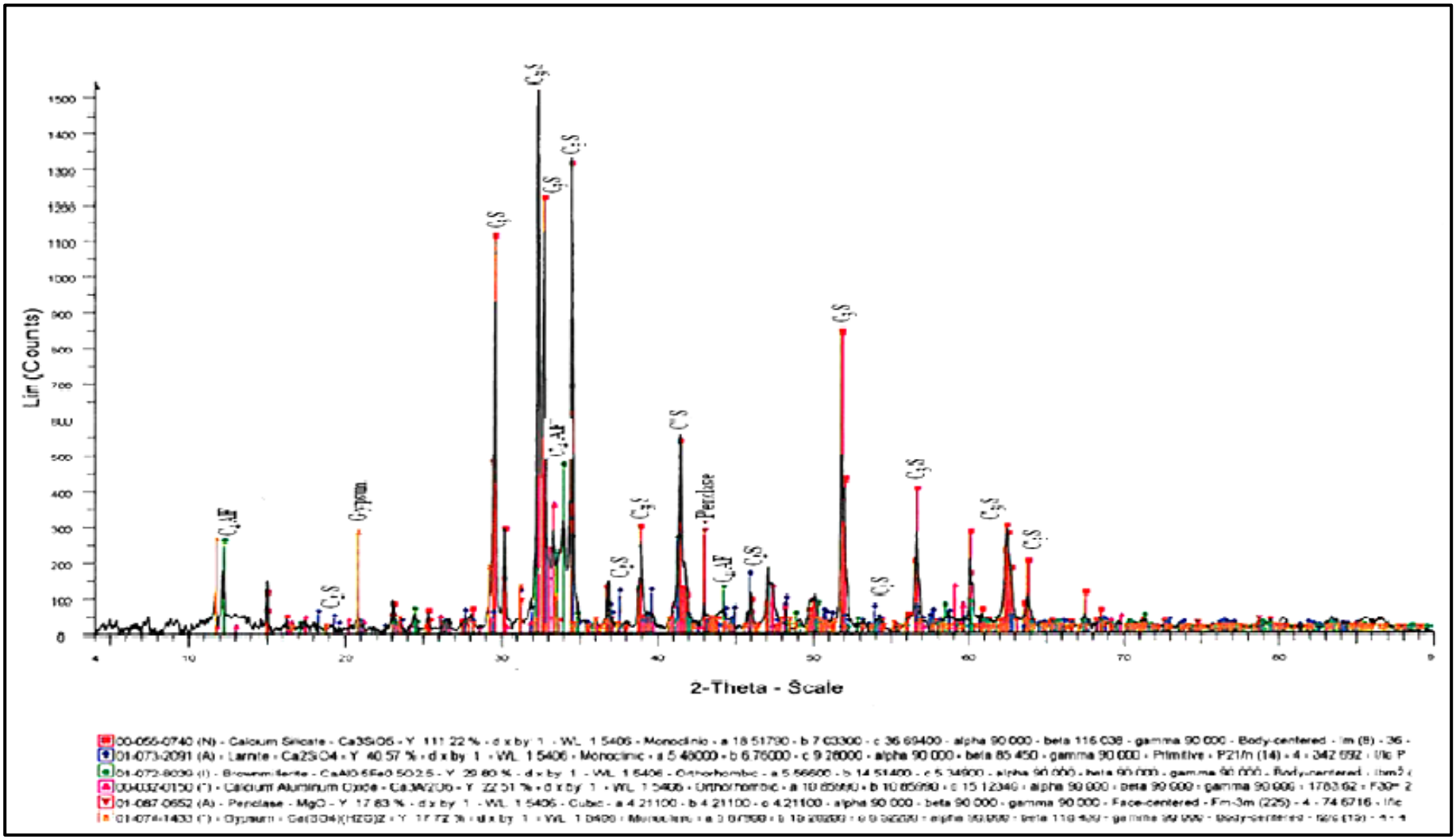


Figure 4.6: XRD trace for Clinker B cement

. The C_2S/C_3S ratio was the almost the same in both the XRD and the modified Bogue calculation for clinkers. Significant differences were observed for the aluminates, possibly due to the preferential packing orientation of the aluminates when the powdered sample is prepared. This could have given rise to higher peak intensity in one of the crystal directions. The XRD C_3S/C_4AF ratios were almost twice as much as the modified Bogue calculation C_3S/C_4AF ratios for both clinkers.

4.4 Cement performance test

4.4.1 Compressive strength

The graphs in Figures 4.7, 4.8 and 4.9 show the compressive strength test results for the 0.3, 0.4 and 0.5 water to cement (w/c) ratios respectively, as measured on 50mm mortar cube sample. The actual measured data is provided in Appendix A.

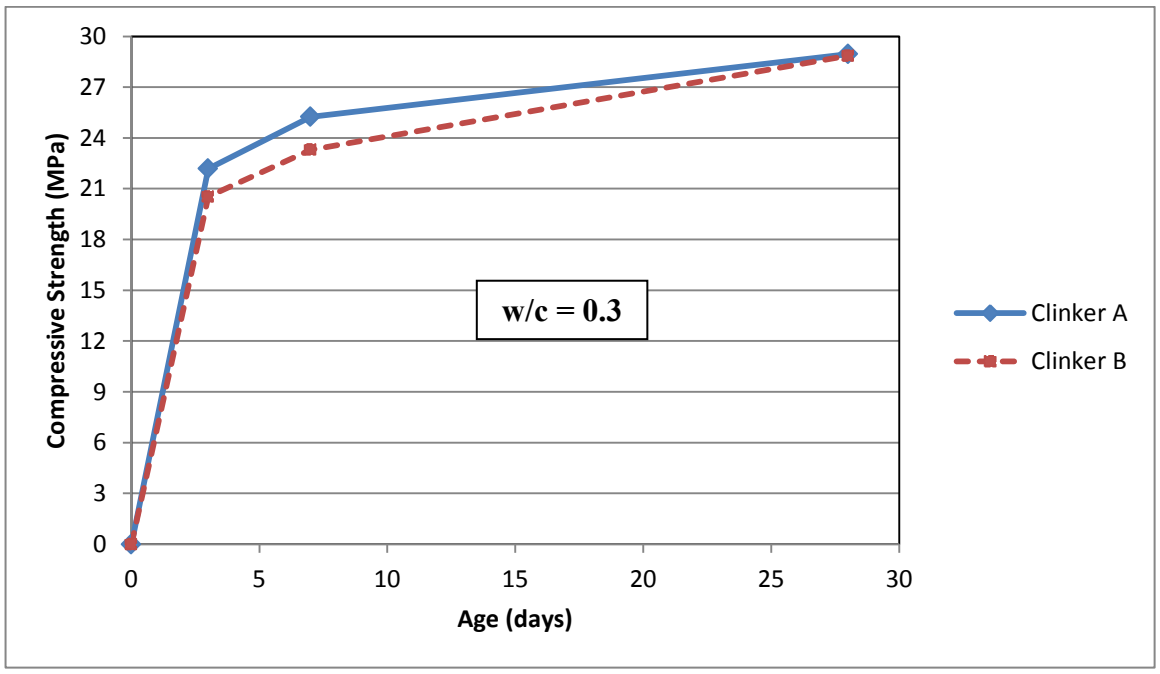


Figure 4.7: Comparative Compressive strength values (w/c = 0.3)

Figure 4.7 shows the graph for the compressive strength development, up to 28 days, of the 0.3 w/c ratio mortar mixtures. The graph shows the mortar strength development of Clinker A and B. Clinker A mortar has a higher compressive strength value than Clinker B mortar

at 3 and 7 day ages. However, at 28 days, the Clinker A and Clinker B mortars showed almost the same strength. The observed strength development trend suggests that the Clinker B mortar strength would surpass that of Clinker A after 28 days. Assuming that the mortar strength gain remains the same as the one between 7 to 28 days, Clinker B mortar strength would exceed that of Clinker A at approximately 30 days.

Figure 4.8 shows the graph for the compressive strength development, up to 28 days, of the 0.4 w/c ratio mortar mixtures. Similar to the strength development for the 0.3 w/c ratio, Clinker A mortar was observed to give higher compressive strength values than Clinker B mortar. The difference in strength increases slightly between day 3 and 7 but is then reduced as day 28 approaches.

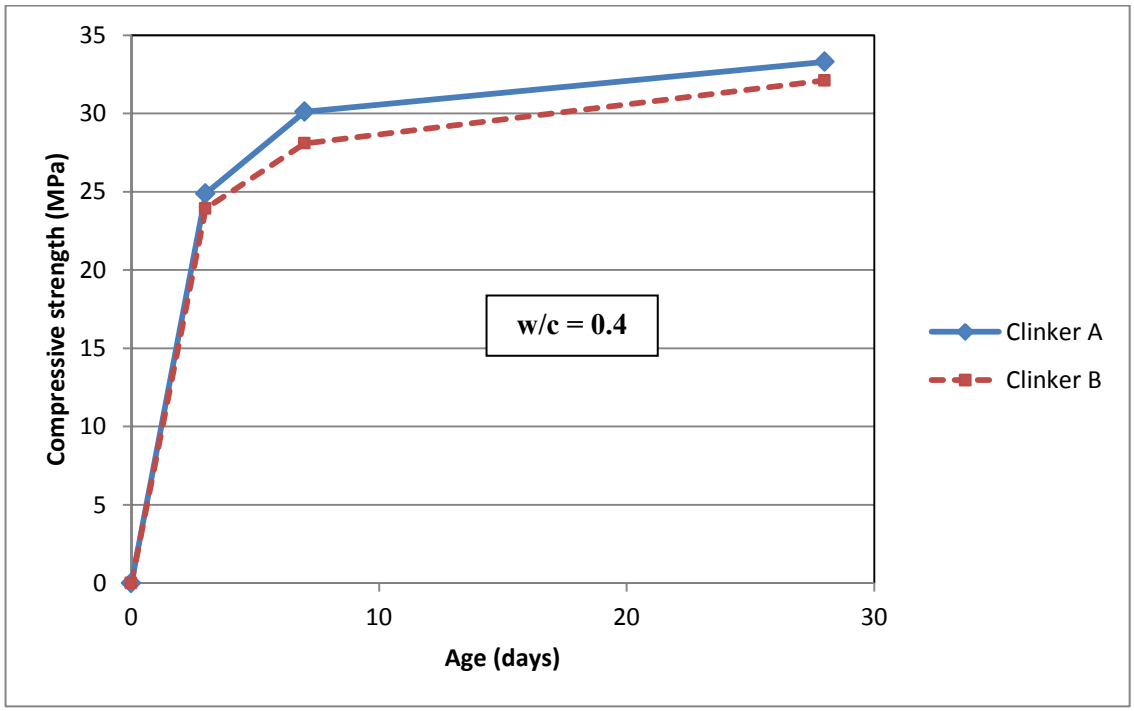


Figure 4.8: Comparative Compressive strength values (w/c = 0.4)

The strength difference between the two mortars varies for each of the test days, with the highest difference at 7 days and the least at 3 days. Clinker A's rate of mortar strength gain decreased more with increase in age. Clinker A's mortar strength gain dropped from 5.2

MPa (for 3 days to7 days) to 3.2 MPa (for 7 days to 28 days), while that of Clinker B mortar remained constant. Assuming that the rate of mortar strength gain remains the same as the one between 7 to 28 days, Clinker B mortar strength would exceed that of clinker A at approximately 60 days.

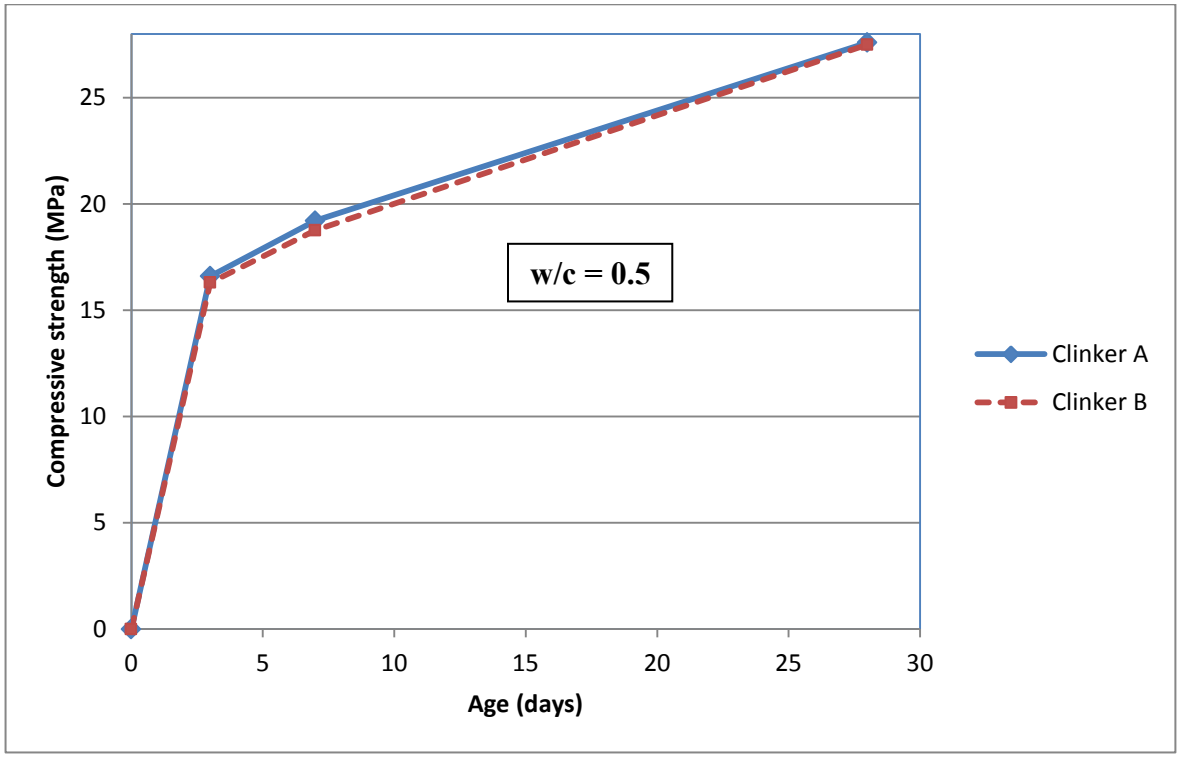


Figure 4.9: Comparative Compressive strength values (w/c = 0.5)

The comparative compressive strengths curves for the 0.5 w/c ratio mortar mixture are shown in Figure 4.9. The Clinker A mortar showed slightly higher strength values than the Clinker B mortar. The difference between the two mortar strengths was much smaller than for the lower w/c ratio mixtures. The rate of mortar strength gain of Clinker A and B were approximately the same at all the testing ages. Assuming that the rate of mortar strength gain remains the same as the one between 7 to 28 days, Clinker B mortar strength would exceed that of Clinker A at approximately 35 days.

4.4.1.1 Compressive strength discussion

The 0.4 w/c ratio mortar mixture yielded the highest compressive strength, which was not expected. The expected result was for the 0.3 w/c ratio mortar mixture to have the highest value. This result concured with Rao (2001) who reports that the Abrams' water/cement law for concrete, which states that compressive strength of concrete is inversely proportional to the w/c ratio, is only applicable to mortar with a w/c ratio greater than 0.4. Rao suggests that this is a result of incomplete compaction due to low workability. At these low w/c ratios, there is also the possibility that hydration ceases in localized areas due to loss of available water for additional hydration or loss of space available for deposition of additional hydration products, because of their higher volume (Lea, 1970). Abram's w/c law was confirmed for the 0.5 w/c ratio mixture, which had a lower compressive strength value than the 0.4 w/c mortar mixture. The variations in strength with w/c ratio are shown in Figure 4.10 and Figure 4.11 for the two clinker cement mortars. The 0.5 w/c ratio mortar mixtures for Clinker A developed strength at a rate much similar to Clinker B, this could be attributed to better hydration condition owing to a higher w/c ratio. In all the compressive strength tests Clinker A behaved as well as a clinker manufactured under normal conditions.

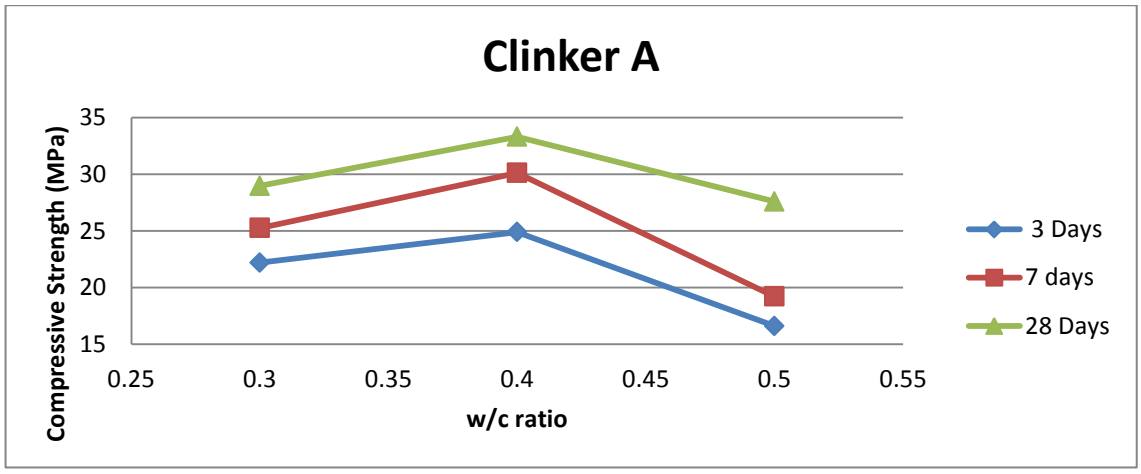


Figure 4.10: Water to cement ratio vs compressive strength variation for Clinker A

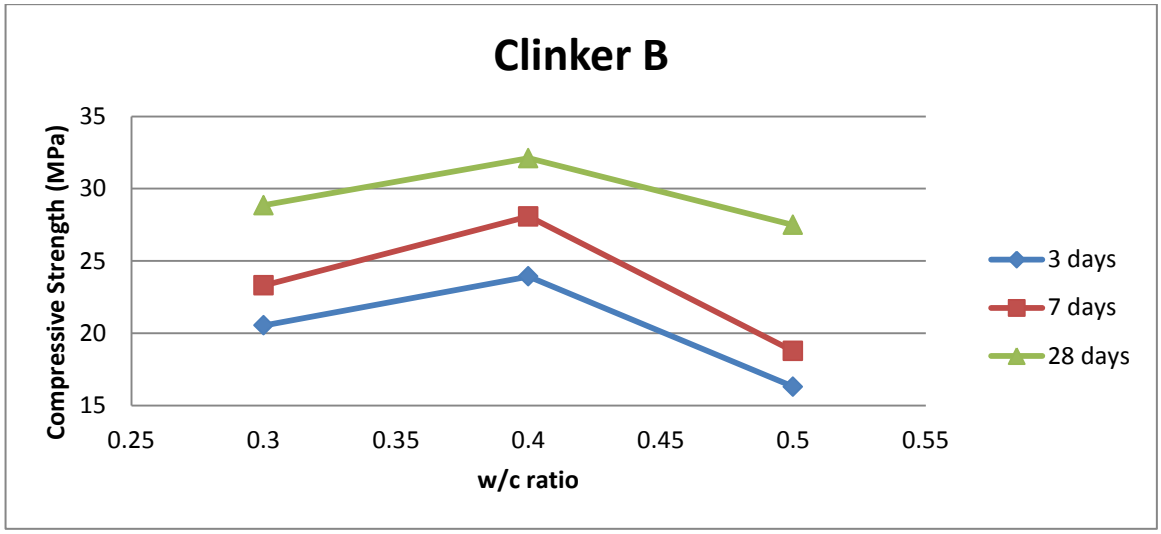


Figure 4.11: Water to cement ratio vs compressive strength variation for Clinker B

4.4.2 Flexural strength

Figure 4.12 shows the flexural strength development graph, up to 28 days, of mortar beams for Clinker A and B mortars. The actual measured data is provided in appendix A.

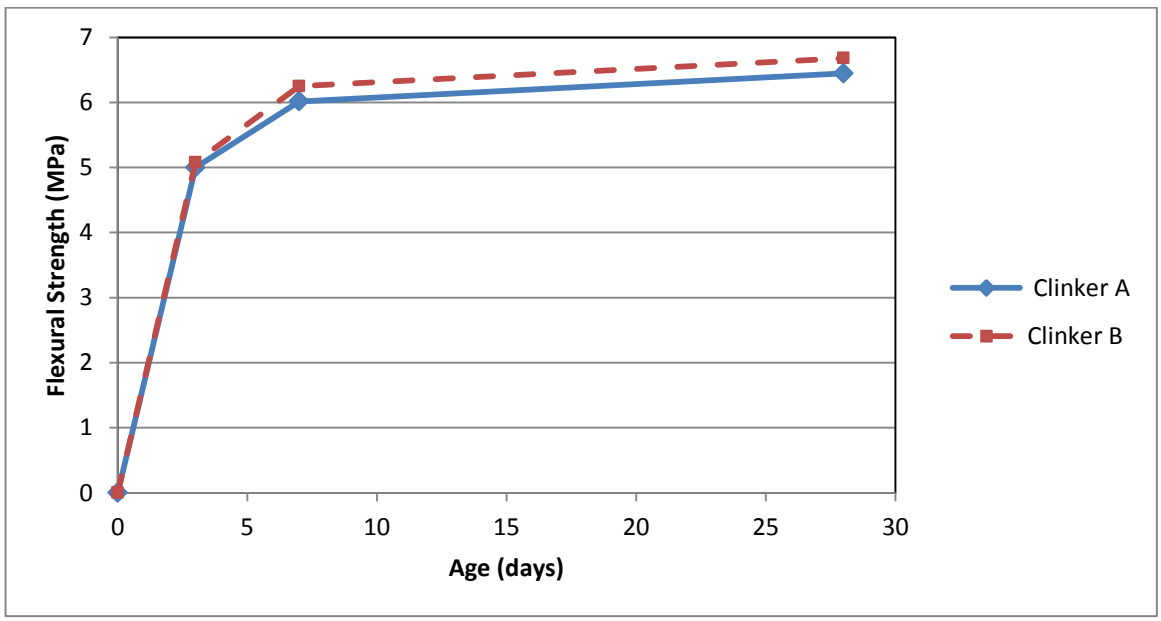


Figure 4.12: Flexural strength development for Clinker A and Clinker B

The test results for day 3 only had a 0.1 MPa strength difference. The strength difference was observed to have increased to 0.3 MPa for the day 7 and day 28 of tests. Clinker B

mortar exhibited a higher rate ofstrength gain than Clinker A between day 3 and 7, with Clinker A mortar mixture having a gain of 1.0 MPa and 1.2 MPa for Clinker B. The two mortar mixtures had the same strength gain of 0.4 MPa, from day 7 to day 28. Clinker A mortar sample performed as well as the conventionally manufactured cement mortar sample. The results corresponded with the results for compressive strength for the 0.5 w/c ratio, where the two mortars behaved similarly. From the flexural strength tests, there is no clear evidence that the tensile strength characteristic of the Clinker A cement has been unduly compromised.

4.4.3 Heat of hydration

The heat of hydration was measured using an adiabatic calorimeter as described in section 3.3.4. The calculated total heat evolved and heat rates are shown in the Figures 4.13 and 4.14. The results are presented in Arrhenius maturity (t_{20}) terms and the actual numerical data is provided in appendix B.

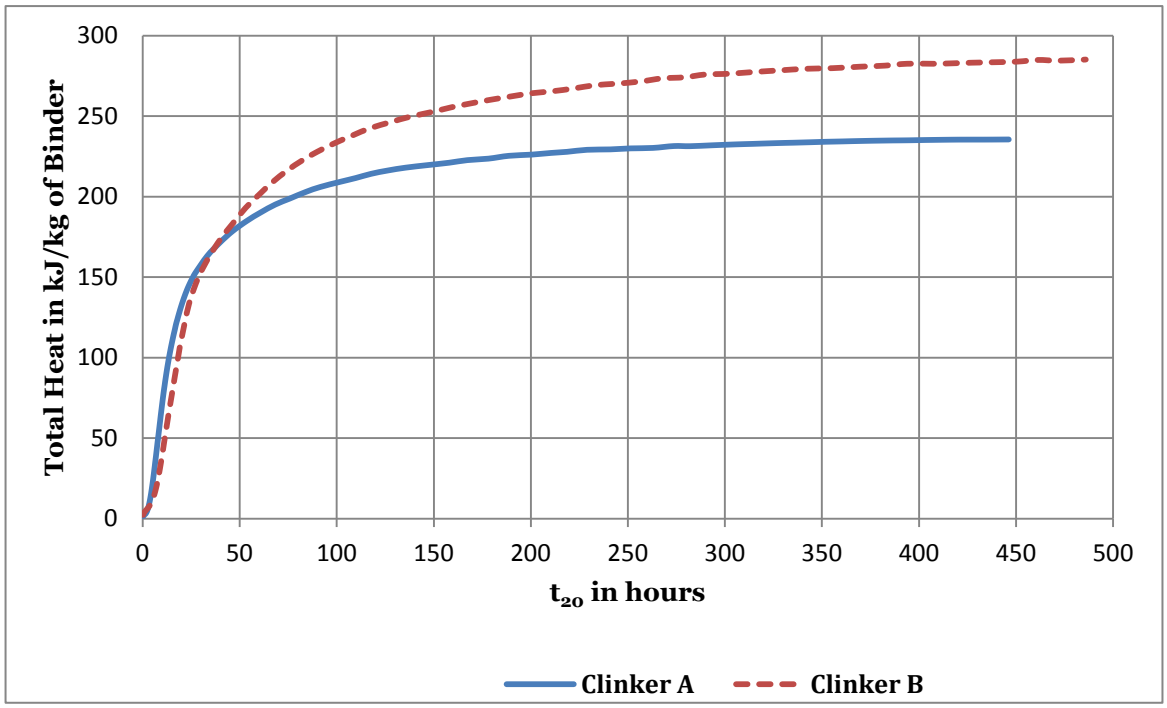


Figure 4.13: Comparative Total heat evolved by Clinker A and Clinker B

From Figure 4.11, it can be noted that Clinker A cement sample had a lower total heat evolution per kilogram of binder than Clinker B. At 446 t_{20} hours, the Clinker A sample had generated approximately 235 kJ/kg of binder while the Clinker B sample had generated 283 kJ/kg of binder. This is a difference of 48kJ/kg or 20 % more than Clinker A. Beyond this point additional heat generation from Clinker A sample was not measurable in the calorimeter. The Clinker B sample continued to generate heat at a low but measurable rate until 485 t_{20} hours to give a total heat of 285 kJ/kg of binder. The difference between the exothermic energy available for the two clinkers can be explained by the different hydration characteristics of the clinkers, resulting from the differences in crystallography and mineral composition. According to Ballim and Graham (2004), this influences the hydration development of cement. Since these two cements were prepared in the same way, the variation can only be attributed to differences in clinker properties. Importantly, the SO_3 content and cement fineness, both known to affect the quantum and rate of heat evolution, were kept the same for the two cements.

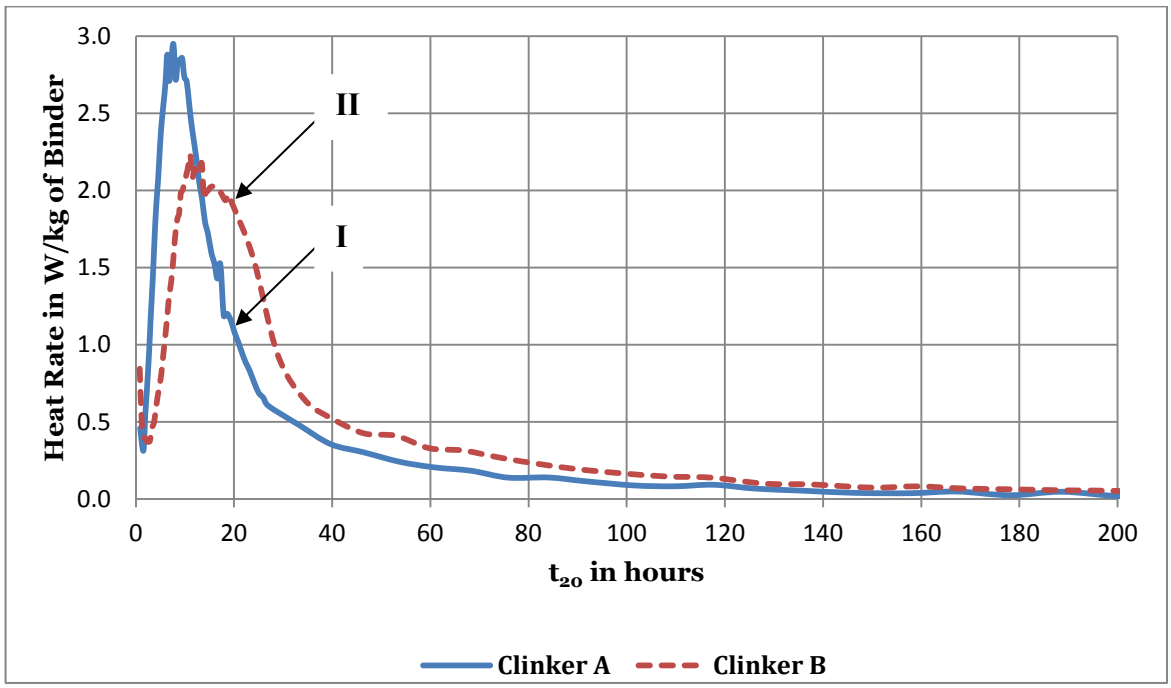


Figure 4.14: Comparative heat rates for Clinker A and Clinker B

Figure 4.12 shows the heat rate curves of the two clinker samples. Clinker A concrete sample was observed to have a higher maximum heat rate (2.94 W/kg) than Clinker B (2.3 W/kg). The peak heat rate for the Clinker A sample also occured earlier (7.64 t_{20} hours) than that of Clinker B (11.09 t_{20} hours). Using Graham's cement classification based on hydration heat rates, Clinker A and Clinker B would be classified as medium and low heat rate clinkers respectively.

The observed difference in the heat rates is not an unusual phenomenon according to work by Graham (2002). Heat rates for South African cements generally ranges between 2 and 3 W/kg and both clinker cements A and B were within this range. Both clinker cement samples showed secondary peaks on the declining limbs of the heat rate curves. The secondary peak for Clinker A cement (**I**) is less pronounced than for the Clinker B cement (**II**). According to Maekawa et al (1999), the secondary peaks can be attributed to the renewed formation of ettringite and /or the conversion of ettringite to monosulphate.

4.4.4 Cement performance tests summary

For the compressive strength tests, Clinker A mortar developed strength at a higher rate than the Clinker B mortar. This trend was more pronounced for w/c ratios below 0.5. For the 0.5 w/c ratio the two cement samples had nearly identical behaviour for both the compressive and flexural strength tests. The strength tests also suggested that, at ages greater than 28 days, Clinker A mortar would have lower strength than Clinker B mortar. The observations from these strength results are reinforced by the heat of hydration test results which show that the Clinker A concrete had a higher quantum and rate of heat evolution than the Clinker B concrete. This means that the hydration process, the process which influences the rate of strength gain, take longer in Clinker B concrete.

4.5 Impact of cement clinker characteristics on concrete structures

In order to quantify the thermal differentials and cracking potential in concrete made from the two clinkers, a 2-dimensional finite difference temperature prediction model developed by Ballim (2004), was used. The measured heat rate profiles were used as input into the temperature prediction model to generate temperature profiles for two hypothetical concrete elements. The two concrete sections used were, one typifying that used in dam wall construction, measuring 4 m wide by 3 m deep with a cement content of 200 kg/m^3; the other being a 500 mm square concrete beam with a cement content of 450 kg/m^3. The two different concrete size elements generate and dissipate heat at different rates because of size and cement content differences. The construction conditions used in the modeling exercise for both sections were as follows (parameters for comparison purposes only):

- The concrete is cast directly upon natural rock with a thermal conductivity of 1,2 W/m.ºC
- The concrete is placed at an ambient temperature (T_A) of 17ºC at 10h00 and the ambient temperature varies sinusoidally (equation 4.1) between 12ºC and 25ºC each day

  $$\boldsymbol{T_A} = -\sin\left(\frac{2\pi(t_d+t_w)}{24}\right)\left(\frac{T_{max}-T_{min}}{2}\right)+\left(\frac{T_{max}+T_{min}}{2}\right) \quad \textbf{4.1}$$ (after Ballim, 2004)

- Timber side formwork is used and is kept in place for 18 hours after casting. The heat transfer coefficient from these surfaces during this time is 5 W/m^2.ºC .
- When the timber formwork is removed, the heat transfer coefficient for the surfaces is taken as 25 W/m^2.ºC.

The measured heat rates of Cements A and B, as shown in Figure 4.14, were used in the numerical model and the comparative results are shown in Figure 4.15 and Figure 4.16.

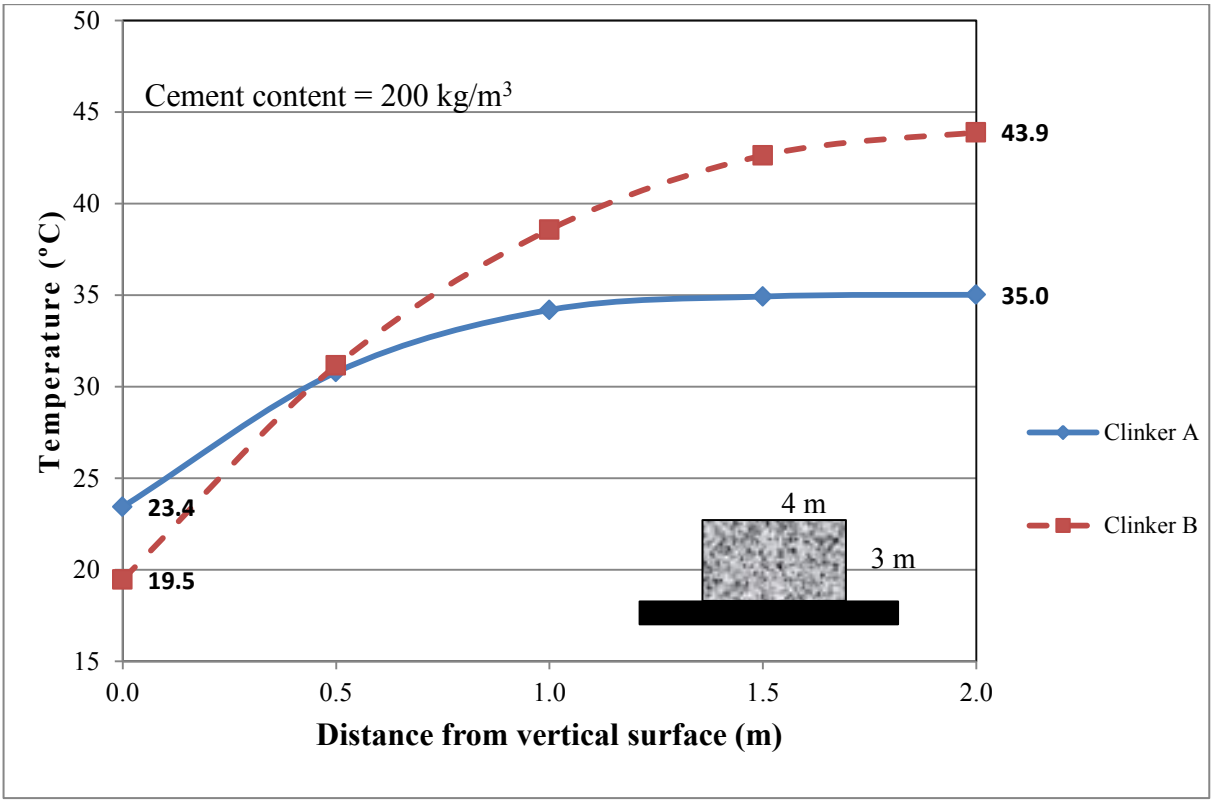


Figure 4.15: Variation in the modeled temperature across a central section of a large concrete block at the time when maximum temperature occurs

Figure 4.15 above shows that Clinker A cement exhibits a lower temperature gradient than Clinker B. Clinker A cement had a maximum temperature gradient of 11.6 ºC which is less than the maximum proposed by Emborg and Bernaders (1994) of 20 ºC. And Clinker B cement had a maximum temperature gradient of 24.4 ºC, which is more than twice that of A and is higher than the recommended maximum. Clinker A cement would be more suited for use in large concrete sections as it results in a lower temperature gradient, making the concrete less susceptible to thermal cracking.

Figure 4.16 shows a small difference between the two temperature profiles for Clinker A and B cements when used in a smaller concrete section with a high cement content. For typical beam and column sections, Clinker A and B cements exhibited similar behaviour. In this case, the maximum temperature difference for Clinker A and B cements was only 1ºC.

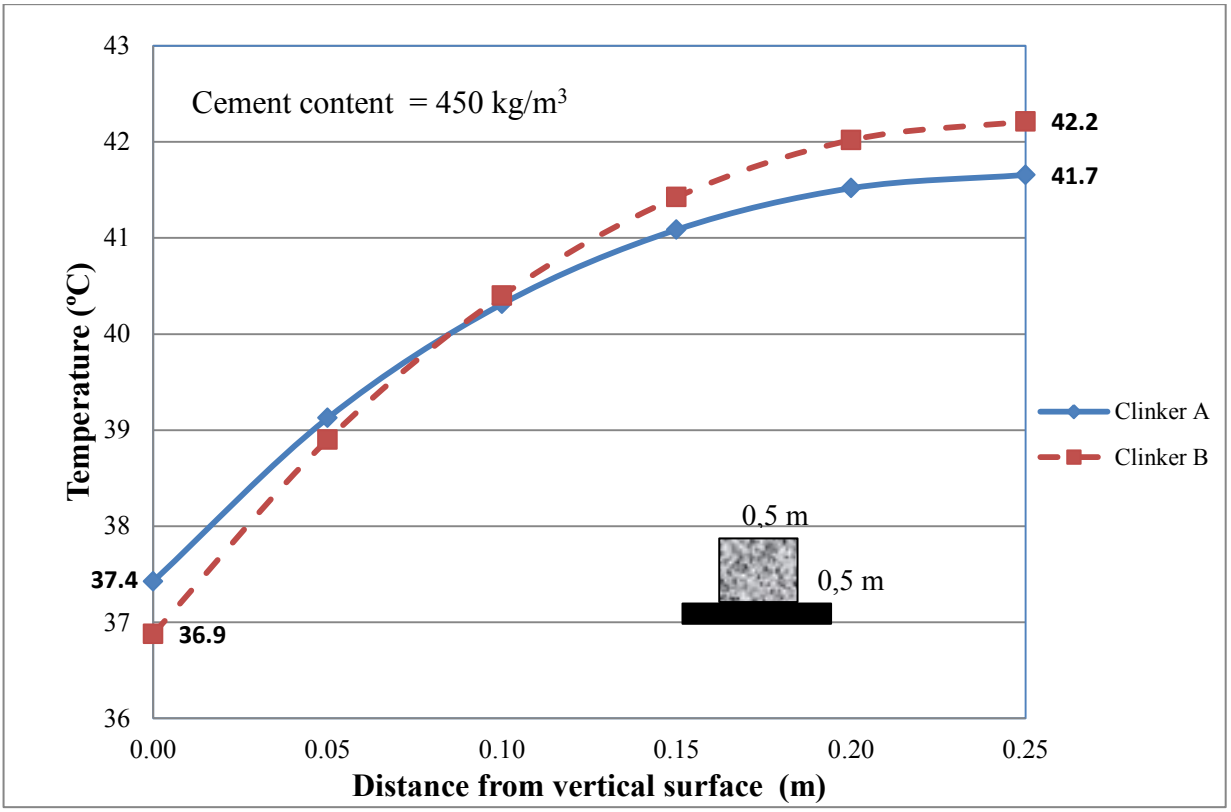


Figure 4.16: Variation in the modeled temperature across a central section of a concrete beam at the time when maximum temperature occurs

The model results suggest that, as produced, Clinker A cement better suited for large concrete structures such as dam walls. However, the Clinker A cement did not significantly change the temperature profile in concrete when used to construct smaller concrete structures, in this case a high strength beam of smaller size.

4.5 Discussion summary

The following important observations are derived from the discussion of all the test results:

- The XRF and Bogue calculation results revealed that the chemical and mineralogical properties of Clinker A were within what is acceptable for cement produced under 'normal' conditions.
- The XRD and the modified Bogue calculation showed that Clinker A cement had a similar mineralogy to Clinker B cement

- The microscopy study revealed major differences between the morphologies of Clinkers A and B. Observations of Clinker A suggested that there may have been incomplete grinding of raw materials, erratic feed of raw materials into the kiln, uncontrolled and fluctuating temperature conditions within the kiln and, finally, unusually slow cooling of the clinker as it exited from the kiln. These factors would, singularly or jointly, have caused the many differences between the two clinkers.
- The strength tests results showed that Clinker A cement matched Clinker B cement strength performance even exceeding that of B in most instances. The tests also showed that the rate of strength gain of Clinker A cement became slower than that of the Clinker B cement as time as time progressed to 28 days.
- The heat of hydration tests showed that for Clinker A cement, the total heat evolved was lower than that of the Clinker B cement but that it had a higher peak heat rate. The heat of hydration characteristic of the Clinker A cement was within the range that typifies Southern African cements.
- The temperature prediction model revealed that the low total heat evolved from the Clinker A cement gave lower temperature gradients and therefore low thermal cracking potential. Clinker A cement performed better than Clinker B cement for use in large concrete structures.

Most of the physical performance results for Clinker A indicated that, despite the evident disruption in the production process, the cement produced from this clinker was not unduly affected. Differences between the two clinkers were most notable in the microscopic assessment. According to Battagin and Maringolo (2008), microscopy allows us to find out what happened during the manufacturing process by studying the clinker morphology. The microscopy study gave an idea of what might have transpired during the disturbed production process. In other tests, the performance of Clinker A was of an acceptable level

and, in some cases, more favourable than the performance of the Clinker B cement. The test results complemented each other e.g. the heat of hydration and strength tests. Clinker A cement had a higher peak heat rate which declined sooner than that of the Clinker B cement. This characteristic was confirmed by the higher rate of early strength gain, that decreased with age relative to that of the Clinker B cement. All the physical test results of the clinker suggested that Clinker A was not significantly affected by the problems experienced during its manufacture. Also similar to the results reported by Graham (2002), there was no clear relationship between clinker morphology and thermal behaviour.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSIONS

To assess the effects of the interrupted manufacturing process on Clinker A, a range of characterization tests of the clinker was undertaken. This characterisation process led to the conclusions below:

1. *The chemical analysis* results showed that the interrupted manufacturing process had not affected the chemical composition of the clinker sufficiently to place it outside the range expected for regular Southern African cement clinkers. The XRD and the modified Bogue calculation showed the mineral composition of the clinker to be within the range specified in the standard (SANS 50197-1) for South African clinkers.
2. *Microscopy investigations* of the apparently atypical clinker showed that its morphology was unusual for a Southern African clinker. This suggests that the clinker morphology had been significantly affected by the interruptions in the manufacturing process. The alite crystals were larger than what is considered normal for cement clinkers and were generally joined, which is typical of slowly cooled clinkers. The microscopy showed signs of unstable crystal growth, with many inclusions and irregularly shaped crystals. The evidence from the microscopy strongly suggested that the clinker may have been slowly cooled, which is uncommon for Southern African clinkers according to Graham (2002). The differences observed in Clinker A may have been a result of a number of factors like incomplete grinding of raw materials, erratic feed of raw materials into the kiln, uncontrolled and fluctuating temperature conditions within the kiln and, finally, unusually slow cooling of the clinker as it

exited from the kiln. These factors may have individually or collectively contributed to these observed differences.

The results for tests carried out to assess the impact of the affected clinker on cement performance led to the following conclusions:

1. The atypical morphology of the clinker did not have a noticeable impact on the mortar compressive and flexural strength performance of the resulting cement clinker. Clinker A cement satisfied the cement standard specifications for strength (SANS50197-1 and ASTM C1329) and generally performed as well as the reference clinker.
2. The heat of hydration results placed the cement within the range of what Graham (2002) reported to be normal for South African cements.
3. The temperature development simulation showed the Clinker A cement performance to be better suited for use in large concrete structures from the point of view of the temperature gradients developed.
4. Given that only two cements clinkers were assessed in this study, it was not possible to identify a clear relationship between clinker morphology and the heat of hydration characteristics of the resulting cement.

In conclusion, Clinker A characteristics were found to be both typical and atypical. Its morphology is atypical but its mineralogy and cement performance are not unusual. Thus, the overall effects of the interrupted manufacturing process on the clinker can be considered as minimal, in engineering use terms, since they have not affected the performance of the final product (the cement).

5.2 RECOMMENDATIONS

For further investigations the following are recommended:

1. Investigate the impact of the manufacturing effects on other cement properties like setting-time and soundness.
2. Use admixtures to improve the workability of the mixture for lower w/c ratios in order to adequately assess the behaviour of the mortar at lower w/c ratios.
3. Investigate the long term impact of the atypical aspects of the clinker on mortar strength by testing the mortar cubes at ages longer than 28 days.
4. Check the quality of clinker produced from the same plant under normal conditions and compare with those of the apparently atypical clinker.

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APPENDIX A

MORTAR STRENGTH RESULTS

CLINKER A COMPRESSIVE STRENGTH

0.5 w/c Mortar Mix

		1	2	3	Mean
3 days	Maximum load (kN)	41.6	40.4	42.5	41.5
	Compressive strength (MPa)	16.64	16.16	17.00	**16.6**
	Deviation	0.04	0.44	0.40	
	% deviation	0.24	2.65	2.41	
7 days	Maximum load (kN)	49.7	46.8	47.6	48.0
	Compressive strength (MPa)	19.88	18.72	19.04	**19.2**
	Deviation	0.67	0.49	0.17	
	% deviation	3.47	2.57	0.90	
28 days	Maximum load (kN)	69.9	67.6	69.4	68.9
	Compressive strength (MPa)	27.96	27.04	27.76	**27.6**
	Deviation	0.37	0.55	0.17	
	% deviation	1.35	1.98	0.63	

0.4 w/c Mortar Mix

		1	2	3	Mean
3 days	Maximum load (kN)	67.5	69.5	64.6	67.2
	Compressive strength (MPa)	27	27.8	25.84	**26.9**
	Deviation	0.12	0.92	1.04	
	% deviation	0.45	3.42	3.87	
7 days	Maximum load (kN)	74.2	76.4	75.2	75.27
	Compressive strength (MPa)	29.68	30.56	30.08	**30.1**
	Deviation	0.43	0.45	0.03	
	% deviation	1.42	1.51	0.09	
28 days	Maximum load (kN)	81.3	80.1	88.7	83.3
	Compressive strength (MPa)	32.5	32.12	35.48	**33.33**
	Deviation	0.81	1.33	2.14	
	% deviation	2.44	4.0	6.44	

0.3 w/c Mortar Mix

		1	2	3	Mean
3 days	Maximum load (kN)	53.60	54.30	58.50	55.47
	Compressive strength (MPa)	21.44	21.72	23.40	**22.19**
	Deviation	0.75	0.47	1.21	
	% deviation	3.37	2.10	5.47	
7 days	Maximum load (kN)	60.00	64.30	65.10	63.13
	Compressive strength (MPa)	24.00	25.72	26.04	**25.25**
	Deviation	1.25	0.47	0.79	
	% deviation	4.96	1.85	3.12	
28 days	Maximum load (kN)	70.30	72.10	74.80	72.40
	Compressive strength (MPa)	28.12	28.84	29.92	**28.96**
	Deviation	0.84	0.12	0.96	
	% deviation	2.90	0.41	3.31	

CLINKER B COMPRESSIVE STRENGTH

0.5 w/c Mortar Mixture

		1	2	3	Mean
3 days	Maximum load (kN)	40.2	39.9	42.1	40.7
	Compressive strength (MPa)	16.08	15.96	16.84	**16.3**
	Deviation	0.21	0.33	0.55	
	% deviation	1.31	2.05	3.36	
7 days	Maximum load (kN)	46.2	46.8	47.7	46.9
	Compressive strength (MPa)	18.48	18.72	19.08	**18.8**
	Deviation	0.28	0.04	0.32	
	% deviation	1.49	0.21	1.71	
28 days	Maximum load (kN)	70.7	65.4	70.1	68.7
	Compressive strength (MPa)	28.28	26.16	28.04	**27.5**
	Deviation	0.79	1.33	0.55	
	% deviation	2.86	4.85	1.99	

0.4 w/c Mortar Mixture

		1	2	3	Mean
3 days	Maximum load (kN)	58.5	59	61.9	59.8
	Compressive strength (MPa)	23.4	23.6	24.76	**23.9**
	Deviation	0.52	0.32	0.84	
	% deviation	2.173913	1.337793	3.511706	
7 days	Maximum load (kN)	72.6	67.9	70.1	70.2
	Compressive strength (MPa)	29.04	27.16	28.04	**28.1**
	Deviation	0.96	0.92	0.04	
	% deviation	3.42	3.28	0.14245	
28 days	Maximum load (kN)	83.3	82.2	75.3	80.3
	Compressive strength (MPa)	33.32	32.88	30.12	**32.1**
	Deviation	1.21	0.77	1.99	
	% deviation	3.78	2.41	6.19	

0.3 w/c Mortar Mixture

		1	2	3	Mean
3 days	Maximum load (kN)	51.30	52.00	50.70	51.33
	Compressive strength (MPa)	20.52	20.80	20.28	20.53
	Deviation	0.01	0.27	0.25	
	% deviation	0.06	1.30	1.23	
7 days	Maximum load (kN)	58.30	56.20	60.30	58.27
	Compressive strength (MPa)	23.32	22.48	24.12	23.31
	Deviation	0.01	0.83	0.81	
	% deviation	0.06	3.55	3.49	
28 days	Maximum load (kN)	75.80	69.40	71.20	72.13
	Compressive strength (MPa)	30.32	27.76	28.48	28.85
	Deviation	1.47	1.09	0.37	
	% deviation	5.08	3.79	1.29	

CLINKER A FLEXURAL STRENGTH

	Sample	1	2	3	Mean
3 days	Maximum load (kN)	2.1	2.1	2.2	2.13
	Flexural strength, R_f, (MPa)	4.92	4.92	5.16	**5**
	Deviation	0.08	0.08	0.16	
	% deviation	1.56	1.56	3.13	
7 days	Maximum load(kN)	2.6	2.5	2.6	2.57
	Flexural strength, R_f, (MPa)	6.09	5.86	6.09375	**6.0**
	Deviation	0.08	0.16	0.08	
	% deviation	1.30	2.60	1.30	
28 days	Maximum load(kN)	2.8	2.7	2.7	2.73
	Flexural strength, R_f, (MPa)	6.56	6.33	6.33	**6.4**
	Deviation	0.16	0.08	0.08	
	% deviation	2.44	1.22	1.22	

CLINKER B FLEXURAL STRENGTH

	Sample	1	2	3	Mean
3 days	Maximum load (kN)	2.3	2.1	2.1	2.17
	Flexural strength, R_f ,(MPa)	5.39	4.92	4.92	**5.1**
	Deviation	0.31	0.16	0.16	
	% deviation	6.15	3.08	3.08	
7 days	Maximum load(kN)	2.6	2.7	2.7	2.66
	Flexural strength, R_f, (MPa)	6.09	6.33	6.33	**6.3**
	Deviation	0.16	0.08	0.08	
	% deviation	2.50	1.25	1.25	
28 days	Maximum load (kN)	2.9	2.8	2.9	2.87
	Flexural strength, R_f, (MPa)	6.80	6.56	6.80	**6.7**
	Deviation	0.08	0.16	0.08	
	% deviation	1.16	2.33	1.16	

COMPARATIVE COMPRESSIVE STRENGTH RESULTS

water/cement ratio	0.3			0.4			0.5		
Age of Testing (days)	**3**	**7**	**28**	**3**	**7**	**28**	**3**	**7**	**28**
Clinker A	22.2	25.3	29.0	24.9	30.1	33.3	16.6	19.2	27.6
Clinker B	20.5	23.3	28.9	23.9	28.1	32.1	16.3	18.8	27.5
Change in compressive strength		3.1	3.7		5.2	3.2		2.6	8.4
		2.8	5.5		4.2	4.0		2.5	8.7

COMPARATIVE FLEXURAL STRENGTH RESULTS

Age of testing (days)	3	7	28
Clinker A	5.0	6.0	6.4
Clinker B	5.1	6.3	6.7
Change in flexural strength		1.0	0.4
		1.2	0.4

APPENDIX B

HEAT OF HYDRATION RESULTS

TOTAL HEAT AND HEAT RATE FOR CEMENT A AND CEMENT B

Cement A			Cement B		
Time (t_{20})	Total Heat (KJ/kg)	Heat Rate (W/kg)	Time (t_{20})	Total Heat (KJ/kg)	Heat Rate (W/kg)
0.00	0.00		0.00	0.00	
0.34	1.48	1.197	0.29	2.26	2.179
0.76	2.27	0.530	0.76	3.74	0.871
1.32	3.01	0.362	1.17	4.48	0.508
1.65	3.76	0.635	1.66	5.23	0.420
1.91	4.51	0.809	2.19	5.97	0.390
2.28	6.00	1.100	2.71	6.71	0.393
2.58	7.48	1.399	3.14	7.45	0.484
2.93	9.70	1.731	3.53	8.20	0.525
3.23	11.94	2.078	3.86	8.94	0.614
3.50	14.18	2.361	4.16	9.68	0.697
3.82	17.20	2.631	4.43	10.42	0.759
4.10	20.18	2.947	4.90	11.91	0.876
4.35	23.15	3.203	5.30	13.39	1.033
4.65	26.86	3.453	5.65	14.87	1.171
4.93	30.61	3.711	5.97	16.37	1.308
5.20	34.52	4.057	6.26	17.85	1.447
5.47	38.24	3.902	6.52	19.33	1.547
5.76	42.68	4.206	6.89	21.56	1.691
6.04	47.18	4.480	7.21	23.79	1.897
6.33	51.66	4.242	7.51	26.02	2.071
6.61	56.20	4.556	7.80	28.26	2.190
6.87	60.67	4.672	8.07	30.50	2.258
7.13	65.14	4.831	8.33	32.73	2.448
7.39	69.61	4.743	8.65	35.69	2.523
7.66	74.16	4.825	8.97	38.74	2.648
7.92	78.63	4.699	9.27	41.73	2.757
8.19	83.08	4.554	9.56	44.70	2.885
8.47	87.56	4.443	9.84	47.70	3.021
8.76	92.02	4.295	10.13	50.70	2.875
9.01	95.74	4.122	10.40	53.68	3.006
9.27	99.49	4.008	10.67	56.66	3.046
9.54	103.22	3.790	10.94	59.62	3.109
9.84	107.19	3.696	11.20	62.59	3.138
10.14	110.91	3.518	11.46	65.69	3.285
10.44	114.62	3.420	11.74	68.66	2.997
10.69	117.59	3.263	12.00	71.63	3.122
10.95	120.86	3.541	12.26	74.61	3.183
11.24	123.84	2.807	12.51	77.58	3.273
11.53	126.84	2.889	12.82	81.29	3.359
11.84	129.99	2.831	13.12	85.01	3.430

Clinker A			Clinker B		
Time (t_{20})	Total Heat (KJ/kg)	Heat Rate (W/kg)	Time (t_{20})	Total Heat (KJ/kg)	Heat Rate (W/kg)
12.15	132.96	2.680	13.42	88.72	3.498
12.47	135.95	2.555	13.72	92.62	3.532
12.77	138.50	2.411	14.01	96.32	3.551
13.04	140.73	2.292	14.32	100.24	3.585
13.32	142.96	2.193	14.61	104.17	3.738
13.69	145.64	2.007	14.88	107.90	3.745
14.02	147.87	1.856	16.91	133.45	3.498
14.37	150.10	1.792	18.94	150.23	2.301
14.74	152.33	1.668	21.06	163.10	1.687
16.86	163.06	1.405	23.09	173.67	1.447
18.96	171.29	1.089	25.23	183.30	1.252
21.04	178.50	0.965	27.34	192.96	1.269
23.30	184.96	0.792	29.41	200.91	1.064
25.33	190.04	0.694	31.48	208.77	1.058
27.53	195.05	0.634	33.66	216.12	0.933
29.64	198.77	0.490	35.84	222.52	0.818
31.93	202.91	0.503	37.92	227.89	0.717
33.95	205.98	0.422	40.30	233.32	0.634
36.62	209.11	0.326	42.60	238.05	0.570
38.80	211.54	0.310	44.81	242.45	0.555
40.86	214.15	0.351	47.47	246.34	0.405
43.03	216.17	0.258	49.75	249.55	0.390
45.40	217.96	0.211	52.69	252.82	0.310
48.15	219.49	0.154	54.81	255.48	0.349
51.05	221.03	0.147	57.01	257.80	0.292
53.39	222.64	0.191	59.22	259.97	0.273
56.07	223.56	0.096	61.71	262.17	0.245
58.66	225.32	0.188	64.21	264.24	0.229
61.53	226.07	0.073	66.40	265.36	0.143
63.97	227.12	0.118	68.95	267.18	0.199
65.97	227.81	0.096	71.24	269.18	0.241
68.46	229.06	0.141	73.63	270.10	0.108
71.32	229.31	0.024	76.32	271.48	0.142
73.85	229.94	0.070	78.70	273.42	0.227
76.59	230.23	0.029	81.12	274.10	0.077
79.16	231.38	0.125	83.35	275.81	0.213
81.16	231.30	-0.012	85.91	276.29	0.052
83.88	231.86	0.058	88.62	277.40	0.114
86.73	232.43	0.055	91.43	278.42	0.101
88.73	232.73	0.041	94.22	279.40	0.097
91.69	233.21	0.045	96.97	279.77	0.037
93.69	233.46	0.035	99.89	280.68	0.087
95.69	233.73	0.038	102.48	281.33	0.069

Clinker A			Clinker B		
Time (t_{20})	Total Heat (KJ/kg)	Heat Rate (W/kg)	Time (t_{20})	Total Heat (KJ/kg)	Heat Rate (W/kg)
97.69	234.04	0.043	104.82	282.51	0.141
99.69	234.26	0.031	107.56	282.50	-0.001
101.69	234.52	0.035	109.56	282.77	0.038
103.69	234.71	0.027	111.56	283.16	0.053
105.69	234.86	0.021	114.36	283.50	0.034
107.69	234.96	0.014	116.36	283.84	0.048
109.69	235.14	0.026	118.46	284.86	0.135
111.69	235.27	0.017	120.46	284.41	-0.063
113.69	235.37	0.014	123.39	285.11	0.067
115.69	235.39	0.002			
117.69	235.42	0.004			
119.69	235.48	0.009			

Adiabatic Calorimeter: Temperature Measurements

Cement A

				Temperature (ºC)		
Time (days)	**Time (hr)**	**Time (min)**	**Time (s)**	**Sample**	**Tank**	**Ambient**
0	0	0	0	22.816	23.172	20.064
0	0	7	42	22.917	22.926	19.665
0	0	20	40	23.017	23.018	21.443
0	0	45	18	23.123	23.145	20.31
0	1	19	16	23.223	23.34	20.256
0	1	39	2	23.325	23.362	20.045
0	1	54	24	23.426	23.541	20.265
0	2	6	19	23.527	23.556	19.991
0	2	17	0	23.628	23.742	20.276
0	2	26	10	23.728	23.752	20.217
0	2	34	41	23.829	23.923	19.976
0	2	42	12	23.929	23.929	19.916
0	2	49	18	24.029	24.099	19.823
0	2	56	5	24.13	24.1	19.997
0	3	2	21	24.23	24.268	20.054
0	3	7	39	24.332	24.45	19.929
0	3	14	2	24.433	24.452	19.993
0	3	19	21	24.534	24.62	20.189
0	3	24	45	24.635	24.616	20.309
0	3	29	50	24.736	24.769	20.111
0	3	34	19	24.843	24.94	19.897
0	3	39	49	24.943	24.976	19.954
0	3	44	21	25.044	25.124	20.171
0	3	48	58	25.145	25.122	19.992
0	3	53	25	25.246	25.311	20.182
0	3	57	33	25.346	25.314	20.141
0	4	1	38	25.447	25.507	19.931
0	4	5	48	25.548	25.546	20.279
0	4	9	42	25.648	25.675	20.022
0	4	13	46	25.749	25.862	20.123
0	4	17	29	25.85	25.856	20.213
0	4	21	15	25.95	26.031	20.021
0	4	24	51	26.05	26.028	20.329
0	4	28	27	26.15	26.212	20.09
0	4	32	5	26.251	26.252	20.238
0	4	35	36	26.352	26.391	20.092
0	4	39	11	26.453	26.53	20.03
0	4	42	37	26.554	26.525	20.114
0	4	45	57	26.654	26.694	19.99
0	4	49	21	26.754	26.851	20.154
0	4	52	11	26.861	26.872	20.071
0	4	56	2	26.961	27.064	20.168
0	4	59	12	27.062	27.06	19.815
0	5	2	32	27.167	27.28	20.135
0	5	5	44	27.267	27.272	19.924
0	5	8	58	27.371	27.4	20.21
0	5	12	5	27.49	27.537	20.027
0	5	15	50	27.59	27.715	20.167
0	5	18	53	27.691	27.718	20.264
0	5	21	55	27.791	27.891	20.094
0	5	24	54	27.892	27.88	20.38

0	5	27	57	27.993	28.048	20.148
0	5	31	0	28.094	28.093	20.215
0	5	33	50	28.194	28.21	20.244
0	5	36	53	28.294	28.328	19.95
0	5	39	46	28.395	28.482	20.201
0	5	42	42	28.495	28.485	20.061
0	5	45	34	28.595	28.644	19.93
0	5	48	32	28.697	28.752	20.278
0	5	51	26	28.798	28.816	20.274
0	5	54	20	28.898	28.978	20.095
0	5	57	16	28.999	28.966	20.261
0	6	0	3	29.102	29.177	20.305
0	6	2	18	29.204	29.172	20.171
0	6	5	49	29.305	29.326	20.33
0	6	8	40	29.407	29.506	20.122
0	6	11	29	29.507	29.496	20.114
0	6	14	18	29.608	29.656	20.314
0	6	17	5	29.709	29.749	20.234
0	6	19	53	29.81	29.791	20.105
0	6	22	43	29.911	29.968	20.288
0	6	25	26	30.012	30.024	20.226
0	6	27	41	30.121	30.134	20.092
0	6	31	8	30.221	30.341	20.303
0	6	33	46	30.323	30.327	20.432
0	6	36	30	30.425	30.528	20.014
0	6	39	17	30.527	30.512	20.117
0	6	41	58	30.627	30.656	20.327
0	6	44	34	30.729	30.835	20.243
0	6	47	11	30.829	30.836	20.073
0	6	49	42	30.93	31.013	20.224
0	6	52	28	31.031	30.998	20.437
0	6	54	55	31.132	31.187	20.055
0	6	57	37	31.233	31.25	20.17
0	7	0	11	31.334	31.36	20.45
0	7	2	45	31.434	31.467	20.064
0	7	5	18	31.535	31.624	19.91
0	7	7	53	31.636	31.657	20.108
0	7	10	29	31.737	31.811	19.712
0	7	13	13	31.84	31.8	19.848
0	7	15	51	31.94	31.969	20.103
0	7	18	25	32.041	32.152	19.74
0	7	20	59	32.141	32.135	19.889
0	7	23	35	32.241	32.334	20.271
0	7	26	8	32.342	32.317	20.556
0	7	28	41	32.442	32.495	20.328
0	7	31	19	32.543	32.578	20.247
0	7	33	55	32.643	32.678	20.49
0	7	36	0	32.756	32.748	20.575
0	7	39	18	32.857	32.835	20.611
0	7	41	54	32.958	33.002	20.445
0	7	44	35	33.058	33.121	20.044
0	7	47	12	33.161	33.161	20.167
0	7	49	48	33.262	33.346	20.305
0	7	52	34	33.362	33.323	20.427
0	7	55	9	33.462	33.52	20.475
0	7	57	55	33.563	33.612	20.046
0	8	0	52	33.664	33.661	20.153
0	8	3	24	33.764	33.813	20.286

0	8	6	6	33.864	33.93	20.409
0	8	8	45	33.964	33.928	20.436
0	8	11	27	34.065	34.094	19.99
0	8	14	16	34.167	34.258	20.098
0	8	17	4	34.269	34.234	20.26
0	8	19	49	34.37	34.432	20.384
0	8	22	35	34.471	34.505	20.301
0	8	25	22	34.571	34.585	20.024
0	8	28	16	34.672	34.763	20.155
0	8	31	1	34.772	34.735	20.291
0	8	33	54	34.873	34.878	20.42
0	8	36	44	34.974	35.068	20.114
0	8	39	43	35.074	35.036	20.064
0	8	42	31	35.175	35.198	20.21
0	8	45	33	35.275	35.377	20.348
0	8	48	27	35.376	35.346	20.394
0	8	51	28	35.476	35.541	19.976
0	8	54	26	35.578	35.662	20.111
0	8	57	27	35.678	35.649	20.263
0	9	0	36	35.779	35.797	20.393
0	9	3	44	35.881	35.945	20.04
0	9	6	47	35.981	36.044	20.04
0	9	9	56	36.084	36.084	20.213
0	9	13	1	36.184	36.28	20.343
0	9	16	12	36.287	36.245	20.451
0	9	19	25	36.389	36.379	19.978
0	9	22	44	36.49	36.537	20.137
0	9	25	59	36.591	36.716	20.311
0	9	29	15	36.692	36.709	20.397
0	9	32	36	36.792	36.877	19.947
0	9	35	55	36.893	36.927	20.119
0	9	39	9	36.994	36.987	20.276
0	9	42	29	37.094	37.102	20.417
0	9	45	49	37.229	37.267	20.099
0	9	50	31	37.33	37.397	20.167
0	9	54	2	37.431	37.54	20.329
0	9	57	33	37.532	37.51	20.336
0	10	1	3	37.632	37.693	20.031
0	10	4	38	37.733	37.865	20.189
0	10	8	7	37.833	37.814	20.332
0	10	11	38	37.934	37.976	20.446
0	10	15	23	38.034	38.089	20.103
0	10	18	55	38.134	38.249	20.212
0	10	22	34	38.235	38.194	20.356
0	10	26	11	38.335	38.321	20.396
0	10	29	58	38.435	38.464	20.045
0	10	33	45	38.537	38.544	20.207
0	10	37	29	38.637	38.711	20.364
0	10	41	21	38.737	38.774	20.277
0	10	45	11	38.838	38.892	20.059
0	10	49	4	38.94	38.984	20.24
0	10	53	1	39.04	39.139	20.408
0	10	56	45	39.18	39.128	20.005
0	11	2	29	39.282	39.379	20.203
0	11	6	27	39.382	39.36	20.38
0	11	10	19	39.483	39.494	20.044
0	11	14	28	39.584	39.604	20.115
0	11	18	45	39.684	39.753	20.306

0	11	22	55	39.785	39.888	20.39
0	11	27	10	39.889	39.937	20.06
0	11	31	46	39.99	39.953	20.258
0	11	35	59	40.091	40.061	20.432
0	11	39	23	40.215	40.217	20.054
0	11	45	53	40.316	40.314	20.275
0	11	50	20	40.417	40.414	20.388
0	11	54	52	40.518	40.501	20.052
0	11	59	32	40.618	40.611	20.256
0	12	3	59	40.719	40.754	20.395
0	12	8	48	40.819	40.867	20.02
0	12	13	34	40.921	40.992	20.247
0	12	18	21	41.022	41.096	20.427
0	12	23	22	41.123	41.2	20.013
0	12	28	16	41.223	41.278	20.231
0	12	33	13	41.326	41.337	20.422
0	12	38	6	41.468	41.442	20.009
0	12	45	56	41.569	41.658	20.357
0	12	51	19	41.67	41.782	19.926
0	12	56	38	41.771	41.902	20.145
0	13	2	9	41.871	41.969	20.374
0	13	7	55	41.971	42.063	19.992
0	13	13	23	42.072	42.171	20.228
0	13	19	6	42.173	42.258	20.323
0	13	23	19	42.294	42.362	19.999
0	13	32	2	42.435	42.383	20.363
0	13	41	18	42.535	42.555	20.132
0	13	47	51	42.637	42.659	20.385
0	13	54	32	42.737	42.796	20.047
0	14	1	20	42.837	42.89	20.3
0	14	8	5	42.938	42.986	20.497
0	14	15	17	43.039	43.112	20.651
0	14	22	5	43.139	43.124	20.768
0	14	29	19	43.239	43.281	20.864
0	14	36	43	43.339	43.446	20.955
0	14	44	22	43.441	43.517	21.02
0	14	51	49	43.543	43.548	21.098
0	14	56	10	43.646	43.658	21.134
0	15	7	32	43.746	43.78	21.205
0	15	14	27	43.879	43.845	21.248
0	15	26	50	43.98	44.076	21.305
0	15	35	7	44.08	44.204	21.36
0	15	43	54	44.181	44.198	21.377
0	15	52	40	44.282	44.36	21.412
0	16	1	38	44.382	44.376	21.429
0	16	6	52	44.493	44.461	21.457
0	16	22	0	44.593	44.567	21.48
0	16	31	49	44.694	44.725	21.478
0	16	41	41	44.794	44.848	21.506
0	16	51	39	44.894	44.96	21.529
0	17	0	31	45.03	44.987	21.539
0	17	15	42	45.176	45.187	21.539
0	17	32	6	45.276	45.246	21.574
0	17	43	30	45.376	45.438	21.574
0	17	51	42	45.507	45.518	21.578
0	18	9	45	45.607	45.674	21.595
0	18	20	24	45.707	45.771	21.608
0	18	32	54	45.807	45.796	21.608

0	18	44	54	45.908	45.897	21.618
0	18	57	36	46.008	46.084	21.589
0	19	9	13	46.11	46.214	21.613
0	19	23	40	46.212	46.269	21.625
0	19	37	30	46.313	46.323	21.64
0	19	49	4	46.454	46.481	21.635
0	20	6	29	46.58	46.602	21.627
0	20	27	18	46.681	46.695	21.612
0	20	41	29	46.781	46.781	21.643
0	20	55	38	46.882	46.896	21.645
0	21	2	6	46.984	46.907	21.647
0	21	17	49	47.091	47.065	21.66
0	21	41	0	47.191	47.235	21.649
0	21	57	2	47.291	47.256	21.63
0	22	12	29	47.391	47.408	21.652
0	22	27	42	47.491	47.584	21.633
0	22	43	51	47.593	47.658	21.649
0	22	55	52	47.721	47.704	21.632
0	23	18	1	47.859	47.86	21.669
0	23	44	49	47.96	48.078	21.67
1	0	2	4	48.06	48.089	21.679
1	0	15	18	48.191	48.25	21.72
1	0	43	56	48.291	48.276	21.669
1	0	54	47	48.409	48.369	21.706
1	1	19	59	48.547	48.522	21.717
1	1	49	39	48.648	48.649	21.729
1	2	0	15	48.763	48.701	21.722
1	2	31	3	48.863	48.964	21.796
1	2	50	55	48.964	49.034	21.854
1	3	11	10	49.066	49.06	21.908
1	3	31	52	49.226	49.205	21.944
1	3	59	19	49.348	49.267	22.003
1	4	33	31	49.509	49.47	21.961
1	5	1	20	49.628	49.625	21.9
1	5	38	19	49.729	49.85	21.869
1	6	4	46	49.83	49.923	21.86
1	6	17	59	49.942	49.898	21.859
1	6	46	32	50.062	50.115	21.885
1	7	33	28	50.163	49.914	22.131
1	7	55	43	50.29	50.207	22.016
1	8	42	6	50.391	50.382	21.937
1	8	57	28	50.503	50.48	21.965
1	9	46	32	50.603	50.682	21.922
1	9	56	50	50.705	50.752	21.928
1	10	50	17	50.806	50.8	21.936
1	11	21	34	50.906	50.891	21.929
1	11	41	23	51.029	51.052	21.907
1	12	37	5	51.129	51.122	21.884
1	12	57	18	51.247	51.268	21.87
1	13	47	44	51.382	51.396	21.914
1	14	47	45	51.458	51.479	21.869
1	15	27	26	51.561	51.649	21.832
1	16	0	0	51.698	51.636	21.806
1	16	51	45	51.812	51.814	21.817
1	17	43	49	51.926	51.95	21.77
1	18	43	49	51.983	52.022	21.748
1	19	1	52	52.085	52.127	21.766
1	19	54	14	52.187	52.238	21.686

1	20	54	14	52.22	52.248	21.67
1	21	23	57	52.328	52.354	21.651
1	22	23	57	52.364	52.373	21.599
1	23	8	56	52.507	52.521	21.594
2	0	8	58	52.535	52.501	21.739
2	0	46	0	52.649	52.604	19.749
2	1	46	0	52.606	52.585	18.35
2	2	3	12	52.71	52.604	20.967
2	3	3	13	52.743	52.731	21.667
2	3	57	56	52.892	51.979	20.139
2	4	57	57	52.853	52.843	20.042
2	5	23	31	52.961	52.947	20.05
2	6	23	31	52.951	52.964	19.977
2	7	4	8	53.075	52.995	19.988
2	8	4	9	53.086	53.159	20.303
2	8	44	53	53.208	53.166	20.237
2	9	44	54	53.19	53.245	20.041
2	10	39	40	53.324	53.262	20.102
2	11	39	41	53.311	53.392	20.046
2	12	31	40	53.439	53.403	20.431
2	13	31	41	53.426	53.401	20.739
2	13	58	27	53.529	53.481	20.829
2	14	58	28	53.508	53.495	20.892
2	15	58	28	53.567	53.659	20.942
2	16	58	28	53.611	53.585	20.939
2	17	58	28	53.661	53.648	20.937
2	18	41	43	53.761	53.712	20.908
2	19	41	43	53.728	53.796	20.876
2	20	27	21	53.831	53.841	20.838
2	21	27	21	53.796	53.818	20.811
2	22	19	24	53.901	53.862	20.77
2	23	19	24	53.864	53.883	20.732
2	23	50	50	53.967	53.876	20.73
3	0	50	51	53.921	53.941	20.665
3	1	50	51	53.95	53.951	20.542
3	2	50	51	53.921	53.892	20.67
3	3	35	41	54.029	53.934	20.613
3	4	35	41	53.989	54.029	20.565
3	5	20	38	54.09	54.007	20.526
3	6	20	38	54.045	54.125	20.503
3	7	9	42	54.145	54.142	20.463
3	8	9	42	54.099	54.137	20.423
3	9	9	43	54.133	54.169	20.374
3	9	52	36	54.239	54.152	20.352
3	10	52	36	54.183	54.155	20.315
3	11	52	37	54.21	54.254	20.261
3	12	43	48	54.31	54.203	20.233
3	13	43	49	54.258	54.272	20.199
3	14	43	49	54.287	54.292	20.145
3	15	43	49	54.305	54.361	20.106
3	16	43	49	54.327	54.357	20.05
3	17	41	25	54.429	54.4	20.007
3	18	41	25	54.372	54.408	19.959
3	19	41	25	54.392	54.403	19.923
3	20	41	25	54.412	54.442	19.885
3	21	41	26	54.426	54.451	19.83
3	22	41	26	54.446	54.525	19.8
3	23	41	26	54.463	54.449	19.754

4	0	41	27	54.48	54.47	19.729
4	1	41	27	54.505	54.56	19.709
4	2	41	28	54.519	54.533	19.842
4	3	41	28	54.535	54.597	19.921
4	4	41	28	54.555	54.619	19.989
4	5	41	29	54.569	54.613	20.046
4	6	41	29	54.583	54.58	20.027
4	7	41	29	54.595	54.632	19.927
4	8	41	29	54.604	54.691	19.883
4	9	41	30	54.615	54.692	19.838
4	10	41	30	54.629	54.702	19.814
4	11	41	30	54.629	54.653	19.798
4	12	41	31	54.639	54.687	19.769
4	13	41	31	54.654	54.704	19.752
4	14	41	31	54.663	54.728	19.719
4	15	41	31	54.671	54.632	19.701
4	16	41	32	54.683	54.751	19.649
4	17	41	32	54.685	54.723	19.613
4	18	41	32	54.683	54.68	19.572
4	19	41	33	54.687	54.725	19.557
4	20	41	33	54.686	54.713	19.513
4	21	41	33	54.691	54.713	19.494
4	22	41	33	54.694	54.695	19.463
4	23	41	33	54.7	54.691	19.431
5	0	31	32	54.702	54.68	19.422

Cement B

				Temperature (ºC)		
Time (days)	**Time (hr)**	**Time (min)**	**Time (s)**	**Sample**	**Tank**	**Ambient**
0	0	0	0	20.18	19.843	18.742
0	0	3	42	20.283	20.314	18.676
0	0	9	49	20.383	20.474	18.511
0	0	17	17	20.486	20.482	18.419
0	0	28	5	20.587	20.59	18.475
0	0	45	41	20.687	20.728	18.584
0	1	9	55	20.787	20.767	18.707
0	1	39	32	20.888	20.939	18.934
0	2	11	24	20.989	20.998	19.145
0	2	42	43	21.089	21.183	19.35
0	3	8	9	21.189	21.211	19.477
0	3	31	49	21.29	21.261	19.629
0	3	51	51	21.39	21.433	19.743
0	4	9	31	21.49	21.467	19.799
0	4	25	54	21.591	21.585	19.837
0	4	40	17	21.692	21.712	19.885
0	4	54	9	21.792	21.857	19.921
0	5	6	41	21.893	21.876	19.958
0	5	18	6	21.993	21.982	20.009
0	5	29	13	22.094	22.096	20.062
0	5	39	14	22.194	22.206	20.118
0	5	49	8	22.296	22.331	20.15

0	5	58	15	22.396	22.439	20.146
0	6	6	58	22.497	22.548	20.148
0	6	15	21	22.597	22.663	20.177
0	6	23	37	22.697	22.765	20.22
0	6	31	16	22.797	22.881	20.253
0	6	38	41	22.898	22.869	20.291
0	6	45	56	22.998	22.983	20.313
0	6	53	15	23.099	23.076	20.317
0	6	59	47	23.2	23.189	20.345
0	7	6	31	23.3	23.286	20.342
0	7	12	51	23.401	23.398	20.399
0	7	19	1	23.502	23.498	20.412
0	7	24	54	23.602	23.617	20.434
0	7	30	48	23.703	23.719	20.457
0	7	36	9	23.804	23.821	20.464
0	7	42	30	23.905	23.928	20.491
0	7	47	50	24.006	24.029	20.526
0	7	53	26	24.106	24.13	20.572
0	7	58	57	24.207	24.226	20.587
0	8	4	21	24.309	24.309	20.571
0	8	9	43	24.411	24.392	20.587
0	8	14	41	24.511	24.522	20.604
0	8	19	35	24.612	24.625	20.62
0	8	24	40	24.712	24.728	20.615
0	8	29	35	24.812	24.822	20.654
0	8	34	27	24.912	24.928	20.685
0	8	39	9	25.013	25.017	20.672
0	8	44	0	25.114	25.106	20.678
0	8	48	19	25.222	25.2	20.717
0	8	53	44	25.324	25.292	20.71
0	8	58	18	25.425	25.395	20.743
0	9	2	27	25.529	25.489	20.764
0	9	7	30	25.629	25.69	20.778
0	9	11	49	25.73	25.8	20.781
0	9	16	23	25.83	25.925	20.772
0	9	20	39	25.931	25.899	20.796
0	9	25	5	26.031	26.057	20.829
0	9	29	17	26.132	26.1	20.854
0	9	33	32	26.232	26.23	20.881
0	9	37	45	26.332	26.313	20.857
0	9	42	12	26.432	26.416	20.906
0	9	46	19	26.532	26.521	20.911
0	9	50	7	26.639	26.613	20.917
0	9	54	59	26.739	26.709	20.884
0	9	59	4	26.84	26.891	20.923
0	10	2	44	26.945	26.972	20.922
0	10	7	30	27.045	27.052	20.917
0	10	11	35	27.145	27.145	20.912
0	10	15	48	27.246	27.221	20.958
0	10	19	53	27.347	27.322	20.98
0	10	24	0	27.448	27.419	21.001
0	10	28	11	27.549	27.528	20.966

0	10	32	16	27.649	27.618	20.976
0	10	36	14	27.749	27.731	20.999
0	10	40	17	27.851	27.813	21.013
0	10	44	17	27.951	27.921	21.056
0	10	48	15	28.052	28.099	21.056
0	10	52	11	28.152	28.114	21.04
0	10	56	12	28.253	28.253	21.088
0	11	0	13	28.353	28.354	21.076
0	11	4	13	28.455	28.436	21.093
0	11	8	7	28.555	28.607	21.094
0	11	11	58	28.655	28.675	21.101
0	11	15	57	28.756	28.746	21.116
0	11	19	57	28.856	28.834	21.136
0	11	23	50	28.956	28.974	21.176
0	11	27	40	29.074	29.119	21.173
0	11	32	24	29.175	29.191	21.192
0	11	36	17	29.275	29.271	21.205
0	11	40	14	29.376	29.397	21.223
0	11	44	13	29.477	29.523	21.224
0	11	48	17	29.577	29.585	21.223
0	11	52	13	29.678	29.649	21.239
0	11	56	8	29.778	29.83	21.258
0	12	0	4	29.879	29.916	21.271
0	12	3	56	29.979	29.988	21.274
0	12	7	54	30.08	30.056	21.265
0	12	11	41	30.182	30.218	21.3
0	12	15	39	30.282	30.282	21.311
0	12	19	30	30.382	30.373	21.311
0	12	23	13	30.483	30.559	21.309
0	12	26	56	30.583	30.618	21.304
0	12	30	46	30.684	30.673	21.312
0	12	34	23	30.784	30.756	21.32
0	12	38	5	30.886	30.946	21.334
0	12	41	38	30.986	31.028	21.347
0	12	45	30	31.086	31.075	21.341
0	12	49	12	31.187	31.159	21.354
0	12	52	54	31.287	31.333	21.39
0	12	56	23	31.388	31.404	21.391
0	13	0	3	31.489	31.488	21.388
0	13	3	35	31.59	31.57	21.399
0	13	7	15	31.69	31.677	21.411
0	13	10	47	31.79	31.858	21.429
0	13	14	22	31.891	31.945	21.41
0	13	17	53	31.991	32.023	21.416
0	13	21	25	32.092	32.119	21.409
0	13	24	55	32.192	32.201	21.428
0	13	28	29	32.293	32.271	21.449
0	13	32	2	32.393	32.361	21.453
0	13	35	30	32.493	32.56	21.476
0	13	38	54	32.619	32.607	21.471
0	13	43	19	32.72	32.752	21.498
0	13	46	53	32.82	32.802	21.507

0	13	50	17	32.92	33.008	21.542
0	13	53	48	33.021	33.018	21.542
0	13	57	11	33.121	33.15	21.52
0	14	0	43	33.222	33.219	21.553
0	14	3	5	33.323	33.275	21.545
0	14	7	38	33.424	33.401	21.543
0	14	10	55	33.55	33.581	21.56
0	14	15	14	33.651	33.718	21.559
0	14	18	55	33.752	33.785	21.57
0	14	22	18	33.853	33.853	21.573
0	14	25	50	33.955	34.005	21.616
0	14	28	58	34.056	34.025	21.62
0	14	32	12	34.183	34.175	21.607
0	14	36	28	34.285	34.265	21.589
0	14	39	52	34.386	34.452	21.594
0	14	43	12	34.486	34.475	21.62
0	14	46	34	34.587	34.67	21.623
0	14	49	45	34.688	34.659	21.653
0	14	53	2	34.789	34.825	21.674
0	14	56	18	34.89	34.853	21.669
0	14	59	45	34.99	34.994	21.672
0	15	2	57	35.09	35.146	21.664
0	15	6	15	35.191	35.172	21.672
0	15	9	31	35.292	35.289	21.664
0	15	12	48	35.392	35.474	21.674
0	15	16	5	35.492	35.454	21.675
0	15	19	17	35.593	35.615	21.674
0	15	22	36	35.693	35.658	21.693
0	15	25	55	35.796	35.807	21.68
0	15	29	17	35.896	35.968	21.708
0	15	32	35	35.997	35.97	21.709
0	15	35	49	36.098	36.195	21.725
0	15	39	8	36.199	36.172	21.725
0	15	42	27	36.3	36.315	21.727
0	15	45	49	36.4	36.448	21.732
0	15	49	3	36.531	36.469	21.771
0	15	53	41	36.632	36.666	21.765
0	15	56	59	36.733	36.706	21.765
0	16	0	41	36.834	36.81	21.765
0	16	4	8	36.935	36.945	21.778
0	16	7	36	37.035	37.089	21.807
0	16	11	13	37.136	37.194	21.799
0	16	14	53	37.237	37.299	21.795
0	16	18	32	37.339	37.33	21.8
0	16	22	12	37.44	37.455	21.813
0	16	26	9	37.541	37.562	21.813
0	16	29	51	37.641	37.65	21.831
0	16	33	53	37.744	37.758	21.858
0	16	38	8	37.845	37.877	21.848
0	16	42	7	37.945	38.026	21.851
0	16	46	24	38.046	38.101	21.873
0	16	50	29	38.147	38.198	21.875

0	16	54	48	38.249	38.286	21.869
0	16	59	4	38.349	38.364	21.906
0	17	3	35	38.449	38.452	21.901
0	17	8	4	38.549	38.539	21.897
0	17	12	36	38.65	38.629	21.916
0	17	17	11	38.75	38.816	21.909
0	17	22	6	38.851	38.885	21.937
0	17	27	1	38.951	38.939	21.915
0	17	31	58	39.052	39.011	21.933
0	17	36	53	39.152	39.258	21.962
0	17	41	39	39.282	39.266	21.974
0	17	49	6	39.384	39.349	21.977
0	17	54	37	39.484	39.495	21.955
0	18	0	1	39.584	39.555	21.966
0	18	5	38	39.684	39.699	21.991
0	18	11	31	39.785	39.848	22.019
0	18	17	9	39.886	39.856	22.05
0	18	23	20	39.986	39.985	22.049
0	18	27	50	40.105	40.065	22.059
0	18	36	17	40.205	40.214	22.042
0	18	41	2	40.319	40.263	22.052
0	18	49	47	40.42	40.389	22.055
0	18	56	21	40.521	40.481	22.081
0	19	2	57	40.622	40.592	22.134
0	19	9	28	40.723	40.692	22.16
0	19	16	23	40.823	40.797	22.168
0	19	23	21	40.925	40.885	22.2
0	19	30	28	41.026	41.052	22.22
0	19	37	22	41.127	41.147	22.25
0	19	44	41	41.227	41.236	22.277
0	19	51	39	41.328	41.339	22.29
0	19	56	28	41.439	41.38	22.3
0	20	7	40	41.54	41.537	22.312
0	20	15	27	41.641	41.696	22.332
0	20	22	50	41.741	41.76	22.374
0	20	28	23	41.858	41.782	22.362
0	20	39	29	41.958	41.994	22.435
0	20	44	8	42.061	41.981	22.429
0	20	55	40	42.162	42.138	22.104
0	21	3	27	42.263	42.26	22.222
0	21	11	51	42.364	42.388	22.37
0	21	19	50	42.464	42.437	22.195
0	21	28	16	42.565	42.608	22.352
0	21	36	4	42.665	42.651	22.167
0	21	44	53	42.765	42.797	22.336
0	21	53	1	42.865	42.831	22.221
0	22	1	33	42.966	42.961	22.143
0	22	10	22	43.069	43.059	22.276
0	22	19	17	43.17	43.153	22.136
0	22	27	50	43.271	43.272	22.224
0	22	36	3	43.371	43.368	22.313
0	22	44	31	43.473	43.488	22.142

0	22	50	49	43.592	43.629	22.37
0	23	5	10	43.694	43.663	20.102
0	23	15	49	43.794	43.807	17.588
0	23	25	34	43.896	43.865	17.802
0	23	35	23	43.996	44.009	17.895
0	23	43	39	44.133	44.086	17.706
0	23	58	53	44.234	44.244	18.137
1	0	8	55	44.335	44.373	17.928
1	0	19	25	44.436	44.44	17.711
1	0	27	39	44.582	44.528	18.123
1	0	43	5	44.682	44.673	17.55
1	0	52	48	44.782	44.754	18.177
1	0	58	10	44.898	44.924	17.587
1	1	13	31	44.999	44.996	17.73
1	1	23	58	45.1	45.093	17.632
1	1	33	48	45.2	45.19	18.096
1	1	43	42	45.301	45.295	17.881
1	1	53	40	45.401	45.413	17.641
1	2	4	0	45.504	45.516	17.642
1	2	8	45	45.613	45.555	17.712
1	2	25	9	45.715	45.706	17.829
1	2	33	37	45.858	45.801	17.522
1	2	50	1	45.961	45.927	17.628
1	2	54	51	46.066	46.002	17.889
1	3	6	6	46.172	46.16	17.76
1	3	20	26	46.307	46.243	17.718
1	3	37	20	46.407	46.486	17.85
1	3	47	32	46.564	46.461	17.577
1	4	5	32	46.665	46.754	17.787
1	4	11	31	46.779	46.81	17.548
1	4	28	34	46.88	46.883	17.501
1	4	40	13	46.98	47.061	17.579
1	4	50	50	47.081	47.043	17.806
1	5	2	32	47.183	47.172	17.665
1	5	13	50	47.283	47.283	17.45
1	5	24	52	47.383	47.376	17.871
1	5	36	8	47.484	47.436	18.17
1	5	47	37	47.586	47.671	19.287
1	5	59	8	47.687	47.741	19.434
1	6	10	10	47.844	47.775	19.498
1	6	28	18	47.945	47.907	19.679
1	6	40	4	48.045	48.093	19.69
1	6	52	0	48.145	48.244	19.762
1	7	4	22	48.246	48.29	19.812
1	7	16	39	48.347	48.358	19.874
1	7	28	39	48.447	48.445	19.915
1	7	41	15	48.548	48.584	19.919
1	7	53	8	48.648	48.685	19.956
1	8	4	51	48.795	48.764	19.958
1	8	25	9	48.896	48.854	19.78
1	8	36	27	49.039	49.029	19.754
1	8	58	50	49.139	49.208	19.693

1	9	11	51	49.239	49.283	19.713
1	9	25	50	49.342	49.39	19.853
1	9	39	52	49.442	49.45	20.059
1	9	46	16	49.553	49.566	19.835
1	10	10	22	49.653	49.662	19.891
1	10	24	51	49.755	49.73	19.805
1	10	39	42	49.856	49.829	19.959
1	10	52	55	50.004	49.969	20.054
1	11	16	45	50.105	50.073	20.001
1	11	23	9	50.208	50.144	20.007
1	11	50	21	50.309	50.296	19.842
1	12	6	23	50.409	50.401	20.117
1	12	22	10	50.509	50.489	20.177
1	12	39	47	50.609	50.638	19.876
1	12	50	56	50.735	50.685	19.907
1	13	18	42	50.835	50.834	20.079
1	13	36	54	50.936	51.033	20.143
1	13	55	10	51.036	51.098	20.04
1	14	13	28	51.136	51.185	20.177
1	14	31	52	51.237	51.312	20.051
1	14	51	23	51.338	51.298	20.046
1	15	3	33	51.459	51.43	20.054
1	15	35	4	51.56	51.534	20.318
1	15	43	5	51.671	51.676	20.062
1	16	17	57	51.771	51.804	19.99
1	16	38	30	51.872	51.852	20.1
1	16	58	32	51.973	51.944	20.356
1	17	11	33	52.105	52.014	20.286
1	17	50	51	52.206	52.199	20.022
1	18	13	20	52.306	52.362	20.106
1	18	36	12	52.411	52.455	20.178
1	19	3	2	52.512	52.587	20.063
1	19	27	57	52.612	52.611	20.098
1	19	52	20	52.712	52.804	20.021
1	20	5	29	52.838	52.864	20.054
1	20	48	23	53.007	52.994	20.021
1	21	20	13	53.123	53.141	19.995
1	21	52	21	53.24	53.166	20.015
1	22	38	49	53.392	53.358	19.223
1	23	28	25	53.534	53.465	19.309
2	0	23	25	53.634	53.608	19.342
2	0	53	8	53.8	53.775	19.374
2	1	45	16	53.968	54	19.426
2	2	15	53	54.068	54.057	19.427
2	2	55	33	54.178	54.178	19.417
2	3	41	36	54.317	54.219	19.419
2	4	41	36	54.412	54.29	19.462
2	5	19	43	54.565	54.517	19.483
2	6	5	12	54.669	54.605	19.319
2	6	48	25	54.772	54.76	19.257
2	7	48	25	54.838	54.834	19.213
2	8	12	4	54.973	54.943	19.194

2	9	0	45	55.086	54.969	19.174
2	9	45	58	55.19	55.161	19.137
2	10	45	58	55.234	55.197	19.113
2	11	13	27	55.38	55.266	19.11
2	12	9	38	55.491	55.413	19.064
2	13	9	39	55.529	55.56	19.006
2	13	42	26	55.677	55.658	18.994
2	14	41	13	55.792	55.796	18.935
2	15	41	14	55.819	55.78	18.898
2	16	12	39	55.957	55.96	18.851
2	17	12	39	55.988	55.95	18.809
2	17	23	49	56.09	55.982	18.805
2	18	23	50	56.109	56.126	18.775
2	18	39	51	56.209	56.118	18.742
2	19	39	52	56.225	56.281	18.746
2	19	56	46	56.336	56.275	18.724
2	20	56	46	56.356	56.41	18.797
2	21	48	17	56.522	56.497	18.894
2	22	48	17	56.507	56.517	19.035
2	23	14	40	56.626	56.528	19.039
3	0	14	40	56.625	56.691	19.1
3	0	37	34	56.735	56.682	19.121
3	1	37	34	56.751	56.786	19.185
3	2	19	19	56.897	56.849	19.225
3	3	19	20	56.895	56.905	19.286
3	4	19	20	56.938	56.992	19.217
3	5	3	19	57.077	56.983	19.194
3	6	3	19	57.079	57.085	19.221
3	6	42	1	57.201	57.17	19.222
3	7	42	2	57.19	57.226	19.224
3	8	7	21	57.301	57.182	19.239
3	9	7	21	57.292	57.266	19.237
3	9	44	44	57.412	57.387	19.249
3	10	44	44	57.396	57.481	19.25
3	11	21	13	57.524	57.517	19.26
3	12	21	13	57.5	57.592	19.234
3	12	54	38	57.616	57.505	19.232
3	13	54	38	57.589	57.636	19.226
3	14	13	57	57.691	57.632	19.238
3	15	13	58	57.663	57.66	19.21
3	15	36	58	57.764	57.689	19.199
3	16	36	58	57.739	57.845	19.165
3	16	56	32	57.842	57.798	19.14
3	17	56	32	57.802	57.89	19.11
3	18	25	41	57.909	57.819	19.076
3	19	25	41	57.878	57.886	19.08
3	19	45	46	57.978	57.917	19.077
3	20	45	46	57.946	57.983	19.076
3	21	13	19	58.051	57.976	19.084
3	22	13	19	58.01	58.054	19.181
3	23	13	20	57.987	58.083	19.714
3	23	58	27	58.099	58.079	19.602

4	0	58	27	58.06	58.057	19.411
4	1	13	54	58.163	58.095	19.406
4	2	13	54	58.131	58.19	19.4
4	2	53	15	58.239	58.157	19.423
4	3	53	15	58.184	58.124	19.63
4	4	53	15	58.202	58.284	19.428
4	5	28	45	58.309	58.197	19.449
4	6	28	45	58.271	58.236	19.482
4	7	10	18	58.384	58.345	19.509
4	8	10	18	58.325	58.325	19.522
4	8	49	3	58.432	58.315	19.527
4	9	49	3	58.377	58.387	19.54
4	10	33	31	58.487	58.466	19.54
4	11	33	31	58.43	58.44	19.53
4	12	33	31	58.456	58.506	19.537
4	13	33	32	58.467	58.545	19.497
4	14	33	32	58.492	58.5	19.482
4	15	33	33	58.519	58.549	19.464
4	16	33	33	58.531	58.56	19.431
4	17	21	41	58.64	58.604	19.409
4	18	21	41	58.565	58.549	19.34
4	19	21	41	58.58	58.617	19.331
4	20	21	42	58.612	58.698	19.331
4	20	50	30	58.716	58.707	19.398
4	21	50	31	58.648	58.605	19.312
4	22	27	48	58.75	58.754	19.33
4	23	27	49	58.676	58.767	19.364
5	0	27	50	58.689	58.374	19.876
5	1	27	50	58.697	58.725	19.719
5	2	23	10	58.823	58.703	19.795
5	3	23	10	58.784	58.917	19.891
5	3	23	28	58.785	58.917	19.902