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**STUDIES ON THE EFFECT OF SELECTED LOCAL
ADMIXTURES ON ESSENTIAL PROPERTIES OF
CEMENT FOR HOUSING CONSTRUCTION**

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**A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE AWARD OF DEGREE OF
DOCTOR OF PHILOSOPHY**

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I hereby declare that this submission is my own work towards the PhD and that, to the best of my knowledge, it contains no materials previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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ABSTRACT

Current trend in cement production is to introduce inorganic admixtures to improve the technical properties such as workability and reduced cracks in concrete. In addition, replacement of clinker or cement greatly reduces environmental pollution due to release of greenhouse gas emissions such as carbon dioxide, carbon monoxide, Nitrogen oxides (No_x) and Sulphur dioxide (SO_2) during cement production. Cement replacement also reduces the high energy cost associated with clinker production and this leads to reduced price of cement.

The objective of this study was to determine the effect and suitability of four local inorganic materials; namely, clay, limestone, clam shells and steel slag (all obtained in Ghana) as mineral admixtures in cement for construction purposes. Blended cements, ranging from binary to quaternary mixes, were produced.

The soundness of the blended cement samples were less than 2.0mm. Water permeability tests showed clearly that addition of the admixtures, except slag, reduced the porosity of the cement by at least 4% and as much as 20%. The water demand of the blended cements ranged from 24.5% to 34.5% and that it increased as the percentage replacements of cement were increased. The water demand of the blended cements ranged from 24.5% to 34.5% and that it increased as the percentage replacements of cement are increased. The setting times of all the blended cements were within the standard limits.

The infrared spectrometry, X-ray Diffraction(XRD), Scanning Electron Microscopy/Energy Dispersive X-ray (SEM/EDX) and Thermogravimetric (DTA/TG) analysis of the study clearly showed that the presence of the four admixtures reduced Ca(OH)_2 content considerably and improved impermeability of concrete. The Infrared analysis indicated that when the admixture content was increased from binary to ternary the accelerating effect of admixtures on hydration was enhanced. This effect manifested in high early strength of the blended cement, especially the CaCO_3 -based blended cement samples. The ettringite and monosulphonate of CaCO_3 -based admixtures (that is, limestone and shell cement) bands were almost flat or disappeared compared to others, indicating increased reactivity between CO_3^{2-} and SiO_4^{4-} ions.

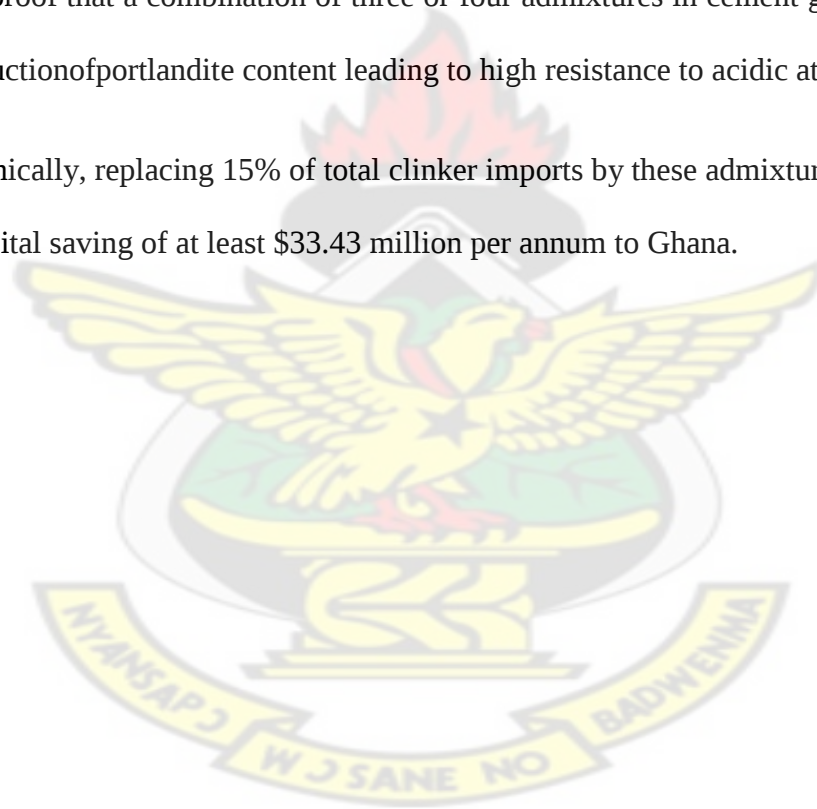
Significantly, the study showed that a combination of three admixtures (5% each) or all four (2.5% each) in the cement almost eliminated portlandite content as compared to 36.9% in the reference cement as provided from the X-ray diffraction (XRD) analysis. This is a novel revelation and it was sufficiently corroborated by the EDX and TG/DTA analysis. The EDX and X-ray analysis also showed increased silica and oxygen composition of the blended compared to the control indicating increasing amounts of calcium silicate components.

The mortar compressive strength tests showed that blending 5%*x*, 5%*x*5%*y*, 2.5%*x*2.5%*y*2.5%*z* and 2.5%*x*2.5%*y*2.5%*z*2.5%*p* by mass of the admixture(s) produced Class 42.5N cement. These cements can therefore be used for early strength concrete

works and all types of construction works. 1:2:4 blended cement concretes with water cement ratio of 0.6 reached the targeted strength value of 20 ± 2 MPa at 28 days.

The study showed that the effect of seawater (NaCl) and Na_2SO_4 on strength was reduced as the number of admixtures in the cement were increased. In all, the quaternary (2.5%x2.5%y2.5%z2.5%p) cement provided the best blend that could resist the deleterious effect of both seawater and sulphate solution negative action. These give ample proof that a combination of three or four admixtures in cement greatly influenced the reduction of portlandite content leading to high resistance to acidic attack.

Economically, replacing 15% of total clinker imports by these admixtures would amount to a capital saving of at least \$33.43 million per annum to Ghana.



DEDICATION

I dedicate this Thesis to my only daughter, Aba Pokuaa Atiemo



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CHAPTER ONE

INTRODUCTION

Portland cement production has traditionally involved calcination of limestone and siliceous clay to produce clinker, which is then interground with 3-5% gypsum. It could contain no more than 5% additives or admixtures. However, current trends in cement production involve the addition of minor constituents, also called admixtures, in order to improve the technical properties and durability of cement as a result of the prevailing climatic (such as high temperature differentials), and/or environmental situation. It is also aimed at reducing carbon gases emission to protect the global environment. Admixture composition could be up to 25% - 70% depending on the type of admixtures.

Cement used in Ghana is mainly Portland limestone cement with limestone content between 18% and 25%. Limestone is obtained locally but the clinker and gypsum are imported from Middle East and Europe. Research studies and commercial production elsewhere make use of fly ash, granulated blast furnace slag, among others, in cement production and have been found to have some technical advantages over ordinary Portland cement such as improved workability, sulphate resistance, reduction in concrete cracks and silica alkali reaction, among others. Ghana abounds in several mineral admixtures which researchers have found to be suitable as ingredients in cement such as clay, limestone, clam shells, bauxite waste, steel slag, iron ore and rice husk among others (Tsakiridis *et al*, 2008; Kakaliet *al*, 2000; Pèraet *al*, 1999; Atiemo, 1998;

Hammond, 1987; Kesse, 1985). These materials are found in large quantities, produced in sufficient amounts, left untapped or discarded as waste. Of these only *Mankranso* and *GomoaMprumem* clay, and *Oterkpolu* and *Buipe* limestone are used in cement production in Ghana, but the rest have not been considered. Also, most cements are produced as binary cements using only one type of admixtures for production such as pulverized fly ash and blastfurnace slag with high silica and lime content respectively. The production of cement containing three or more admixtures has not gained popularity so it is a vital component of this study. This study looks at the suitability and influence of four local admixtures as vital ingredients in cement production with the aim of reducing cost and carbon dioxide footprints, and making housing delivery cheaper in Ghana. It is also aimed at enriching the knowledge of utilization of industrial waste material and other natural admixtures in cement production.

The study presents a range of materials that are available for use as raw materials in cement for construction. Their utilisation would greatly reduce the cost of a key building material and, therefore, the cost of housing delivery in developing countries with special reference to Ghana.

1.1 Cement additives and Global Environmental benefits

Several research studies have shown that mineral admixtures such as limestone, pozzolana, slag, fly ash, trass, among others, in Portland cement influence hydration of cement and its properties. For limestone fillers, it has been proven that there is interaction between calcium silicate and CaCO_3 and that calcium

carboaluminate hydrates precipitate during hydration of cement containing CaCO_3 . It is also generally accepted that there is a positive effect of limestone on the water demand of the blended cement (Rahhaland Talero 2005; Portland Cement Association, 2004 Pera, *et al* 1999).

The world's production of cement in 2006 exceeded 2.6 billion tonnes (Cement Global report, 2007). This means an evolution of about 2.6 billion tonnes of carbon dioxide (CO_2) during clinker production since production of one tonne of clinker releases about a tonne of CO_2 . Therefore, the addition of mineral admixtures or fillers and consequent reduction of the clinker in ordinary Portland cement production provide both economic and environmental benefits. Based on Portland Cement Association calculations (2004), using 5% limestone in cement production in 2006, the environmental benefits would include:

- reduction in energy consumption of about 6.6×10^6 MW-hr;
- reduction in carbon dioxide emissions of more than 5 million tonnes; or by approximately 5 percent per ton of cement produced;
- reduction of cement kiln dust of above 450,000 tonnes;
- reduction in raw materials use of 4.0 million tonnes; and
- considerable reduction of NO_x and SO_2 emissions from reduced fuel consumption.

As a result, addition of admixtures leads to significant reduction of greenhouse gas emissions such as carbon dioxide, carbon monoxide, methane or chlorofluorocarbons

(from fossil fuels). Partial substitution of Portland cement with admixtures/fillers also reduces the cost of cement production thus impacting positively on price of cement.

1.2 Cement Industry

The construction industry is a vital sector of any economy since infrastructural development forms one of the indicators used in measuring a country's development. Cement undoubtedly is one of the most essential commodities in the construction sector. An in-depth analysis by Global Cement Report (2007) showed that cement consumption in 2006 was about 2.56 billion metric tonnes but shot to 2.86 billion tonnes in 2009, an increase of 12%. Consumption continues to rise globally due to increased infrastructure development despite its high price, especially in third world countries. China is the largest producer of cement in the world, accounting for almost 47% of the world's total output producing about 1.4 billion tonnes. The growth of cement consumption in China was measured at between 9% and 14% from 2005 to 2008, representing an increase of 1.05 billion metric tonnes in 2005 to 1.4 billion tonnes in 2008. In India, the second largest world's consumer, cement production, buoyed by a strong demand, increased to 183 million tonnes in 2008. In the United States, the demand levels of cement reached a peak of about 122million tonnes in 2006 but declined to 100 million tonnes in 2008. Globally, cement production has increased appreciably by 30.5% from 2.2 billion tonnes in 2004 to 2.86 billion tonnes in 2008, West and North Africa constituted about 4% of global consumption of cement as compared to 1% for South and Central Africa in 2008 (Cement Global Report, 2009, 2010).

Across Africa, there have been positive increases in cement production and consumption. Nigeria consumed an estimated 14.8 million tonnes in 2009, giving a per capita consumption of 98kg, compared to about 8.4 million tonnes in 2004 (Access Securities, 2009) whilst Ghana saw a steady rise in cement utilisation from 1.8 million tonnes in 2000 to about 3.3 million tonnes in 2009, giving a per capita consumption of 133kg (Ghacem Limited, 2010). Despite the increase in the usage of cement worldwide, developing countries continue to experience high costs of the commodity due to low production, high freight cost, weak national currencies, and high energy tariffs. Most of the cements used in these countries are either imported wholly or produced from imported clinker and gypsum. Ghana imports all its clinker for the production of ordinary Portland cement whilst Nigeria imports about 43% of its cement requirements (International Cement Review, 2010). Even in countries where cements are produced locally, such as India, Iran, Ethiopia, Nigeria, Togo and Zimbabwe; the high cost of production due to high cost of fuel oil, old machinery and inefficiency in production are some of the reasons for the high prices of cement.

The price of cement has seen approximately 157% increase from year 2001 to 2010 in Ghana, over 55% in Nigeria between 2002 and 2004, and 23% in India in 2003 (Times News Network, 2004; and Omohand Njoku, 2004). It is now retailed between \$8 and \$10 in Ghana, \$7.2 in Ethiopia and Nigeria and about \$4.1 in India per bag of 50kg. This is certainly beyond the reach of the vast majority of people in these developing countries, where income levels are low and about half of the population lives in poverty.

As a result of the afore-mentioned problems of high cost and unavailability of cement, the use of durable local cementitious materials would help to reduce the price of cement in these countries. Several materials exist in Ghana which can be blended with ordinary Portland cement for building and construction without affecting the strength, quality and durability of the cement products. In most cases the quality of the cement is improved and the cost of production greatly reduced.

1.3 Domestic Cement Usage and Demand Analysis

The last study on usage of cement in Ghana in 1996 by Mott MacDonald Consulting Limited showed that the building sector accounted for more than 90% of cement consumption whilst the road sector consumed the remaining 10% mainly for the construction of bridges, culverts, drains, pedestrian pavements, among others. Table 1.1 presents the trend of cement consumption in Ghana from the year 2000 to 2009. It shows that cement usage has increased from 1.8 million tonnes to about 3.3 million tonnes.

Table 1.1: Estimated consumption of Portland cement in Ghana

Year	Cement in million tonnes
2000	1.81
2001	2.05
2002	2.15
2003	2.33
2004	2.50
2005	2.65
2006	2.80
2007	3.02
2008	3.31
2009	3.29

**Sourced from GHACEM and Diamond Cement Ltd (2010)*

Cement consumed in Ghana is produced from imported clinker and gypsum from Togo, Middle East and Europe. Since the year 2008 more than \$280 million is spent annually on clinker and cement importation in Ghana. Cement consumption will continue to increase because of increasing population growth and increased infrastructure developmental activities by the Government, estate developers, institutions and private individuals.

1.4 Technical and Economic Benefits of Using Blended Cements

Technically, the presence of admixtures like limestone, slag and pozzolana in Portland cement influences the rate and degree of cement hydration as well as the phase composition of hydrated cement paste (Klieger, 1990; Hawkinset *al*, 2003). Their addition may increase the hydration rate of clinker minerals and become more pronounced with greater fineness. The formation of ettringite is also enhanced but its tendency to transform to the monosulphate form is diminished. Mineral admixtures also improve the workability of cement, lower the heat of hydration and energy cost, among others. In some instances their presence increases the resistance of the blended cement to acidic water attack.

Ghana utilizes about 3.3 million tonnes of cement annually. Consumption in West Africa exceeds 150 million tonnes, with more than 70% being imported. A reduction of clinker imports by at least 15% substitution with local admixtures will greatly reduce the cost of locally produced cement and environmental pollution. Utilisation of local limestone, clam shells, pozzolana, slag, among others in production of cement will

expectedly decrease the cost of production by at least 10% as a result of energy reduction and reduced cost of materials. It will also result in capital retention and increased technical capacity.

1.5 Main Objective

The objective of this study was to evaluate the suitability of four inorganic materials; namely clay, limestone, clam shells and steel slag (all obtained in Ghana) as mineral admixtures in cement for construction purposes. To achieve this aim, the following properties of the materials were studied:

- Physical properties and chemical composition of reference cement (ordinary Portland cement) and admixtures;
- Chemical composition of blended cements;
- Mineralogical composition of raw samples and blended cements;
- Water demand and setting times of blended cement pastes;
- Drying shrinkage of blended cements;
- Soundness of blended cements;
- Infrared (IR) spectrometry analysis of hydrated cement samples;
- X-ray Diffraction (XRD) analysis of hydrated cement products;
- Scanning Electron Microscopic (SEM) and Energy Dispersive X-ray (EDX) analysis of hydrated cement mortars;
- Thermal analysis of blended cements;
- Compressive strengths of blended cement mortars, concrete cubes and prisms;

- Tensile strengths of concrete using blended cements and Class 42.5N CEM I Portland cement;
- Durability tests of cement products using 5% sodium sulphate and sea water by:
 - determining samples appearance after 365 days;
 - determining the compressive strengths after 365 days;
- The economic benefits to be derived from the addition of local mineral admixtures in Portland cement for housing construction in Ghana.

The specific objectives would be to show the influence of these admixtures on the essential properties of cement. This would include the influence of the admixtures in cement reactions and hydration, precipitation of portlandite $[\text{Ca}(\text{OH})_2]$ and also setting times, soundness and strength even at 20% replacement of cement within the standard limits.

In order to achieve these objectives a literature review would be carried out as well as the study of properties and sources of these admixtures. The materials would be assessed for their suitability using GS, BS, EN, ASTM and ISO Standard Testing Methods. The results so obtained would be interpreted and discussed, and their application in construction stated. The resultant conclusions would be made and the economic benefits from the study evaluated. Finally, relevant recommendations which will improve the important properties of cement and the advantage that will inure positively to Ghanaian economy would be presented.

CHAPTER TWO

LITERATURE REVIEW

2.1 Cement

Cement is defined as finely ground inorganic hydraulic binder which, when mixed with water, forms a paste which sets and hardens by means of hydration reactions and chemical processes and which, after hardening, retains its strength and stability even under water (EN 197-1, 2000). The production of ordinary Portland cement (oPc) involves the calcination of limestone and clay in a rotary kiln to a temperature of about 1400°C. The clinker produced is then interground with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which regulates the setting of cement. Cement has revolutionised the building industry because of its early setting and hardening, and its early strength gain and durability were found to be far superior and better than such materials as lime-pozzolana, lime –sand and lime-soil mixtures/mixes.

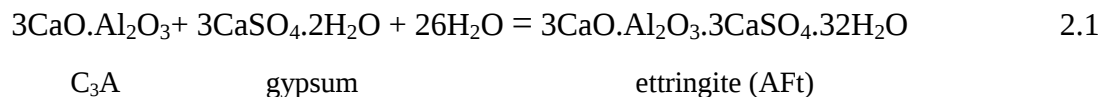
Portland cement is composed mainly of the four clinker minerals, namely, tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$ (C_3S); dicalcium silicate, $2\text{CaO} \cdot \text{SiO}_2$ (C_2S); tricalcium aluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (C_3A); and tetracalciumaluminoferrite (C_4AF) to which 3-5% gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is added. Chemically, CaO , SiO_2 , Al_2O_3 and Fe_2O_3 constitute about 80% of Portland cement. The other significant minor oxides are MgO , SO_3 , K_2O , and Na_2O . Although the amounts of these oxides are relatively small, they affect the hydration process of Portland cement (oPc) and the composition of hydration products (Lea, 1970).

Alite (tricalcium silicate) forms the bulk of clinker, 40-70% by mass, with hexagonal crystal sizes up to about 150µm. It reacts rapidly with water and is responsible for much of the early-age (≤ 28 days) strength development. Belite (dicalcium silicate) forms 15-45% of clinker with rounded crystal sizes ranging from 5 to 40µm. It is less reactive than alite but does contribute to later-age strengths (> 28 days). Upon hydration, both alite and belite form poorly-crystallized calcium silicate hydrates (C-S-H) and well-crystallized calcium hydroxide (portlandite). Tricalcium aluminate constitutes 1-15% of clinker with a particle size of between 1-60µm and occurs as either cubic or orthorhombic form. It is highly reactive with water. Tetracalciumaluminoferrite (Ferrite; C_4AF) constitutes between 1% and 18% of clinker content (Stutzman, 2004).

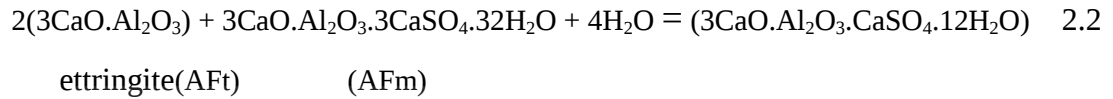
2.1.1 Chemical Reactions and Hydration of Cement

The various particles of cement components react chemically when it mixes with water producing various phases. These reactions are by hydration and hydrolysis of these clinker minerals and gypsum leading to the setting and hardening of the cement. The main reactions of the individual cement compounds that take place sequentially are as follows (Lea, 1970; Zhou, 2006):

- The C_3A reacts with both water and gypsum ($CaSO_4 \cdot 2H_2O$) to produce unstable ettringite (AFt).

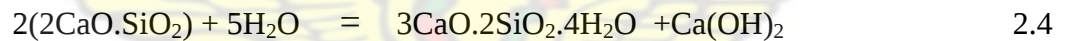


This reaction is responsible for the setting of cement. Once all the gypsum is used up, the ettringite becomes unstable and reacts with the remaining C_3A to produce stable calcium monosulphate aluminate hydrate crystals (AFm).



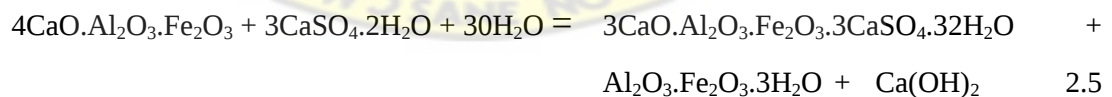
The size of the monosulphate is two and half times that of ettringite.

- The C_3S (alite) and C_2S (belite) react with water in a complete hydration to produce calcium silicate hydrates and calcium hydroxide as follows:

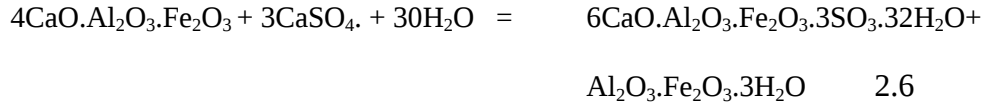


The products of these reactions contribute to the strength of cement products, with C_3S contributing about 75% of it.

- Like C_3A , C_4AF (ferrite) reacts with gypsum and water to form ettringite, lime and alumina hydroxides:



The complete compound is called garnet, which is produced by the further reaction of C_4AF with ettringite.



The above reactions are accompanied by heat liberation. Measuring the liberated heat of hydration is one of the methods of determining the degree of hydration.

2.2.2 Hydration process of Portland cement

The hydration of Portland cement is exothermic. Variation in the liberated heat of hydration mirrors, in one way or another, the hydration mechanisms. The process of hydration can be followed by monitoring the heat evolution by means of conduction calorimetry. Figures 2.1(a) and (b) show a typical heat evolution curve reported by Mindess *et al.*, (1981). Fig. 2.1(a) gives a descriptive narration on the heat evolution. This process can be divided into 4 stages, including the pre-induction (i), dormant (ii), acceleration (iii) and post-acceleration (iv) stages.

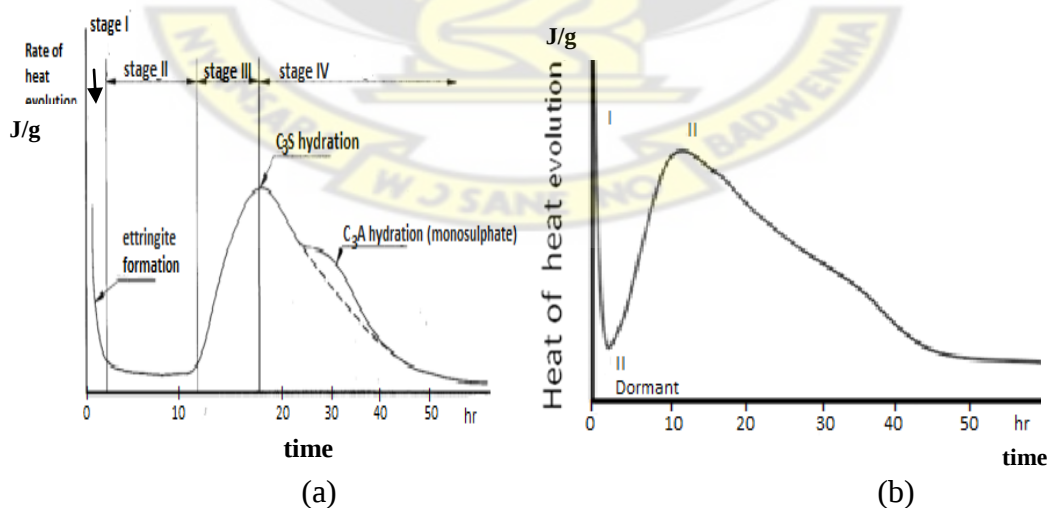


Figure 2.1: Rate of heat evolution (Mindess and Yong, 1981)

2.2.2.1 Pre-induction stage (Stage I)

Almost immediately on adding water, some of the clinker sulphates and gypsum dissolve, producing an alkaline, sulfate-rich solution. Soon after mixing, the (C_3A) phase - the most reactive of the clinker minerals - reacts with the water to form an aluminate-rich gel (Stage I). The gel reacts with sulfate in solution to form small rod-like crystals of ettringite (Eqn. 2.1). Hydration of free lime and the wetting of the cement also occur at this stage (Lee, 1983). C_3A hydration is a strongly exothermic reaction but it does not last long, typically only a few minutes.

The fast heat evolution at the pre-induction period is attributed to the hydration of C_3A , the hydration of free lime and the wetting of the cement (Eqn 2.1). C_3A is the most active at this stage and reacts with gypsum to produce ettringite. The main products are ettringite and calcium hydroxide (Lea, 1970; Zhou, 2006). The duration of this stage is less than 60 minutes. This reaction leads to the initial setting time of cement.

2.2.2.2 Dormant stage (Stage II)

The dormant or induction stage follows stage I, and is characterized by a period of about two hours of relatively low heat evolution. Here, cement exhibits low reactivity. The first part of the dormant period – up to perhaps half-way through - corresponds to when concrete can be placed. As the dormant period progresses, the paste becomes too stiff to be workable. The final setting time is achieved within this stage.

Two of the most often mentioned concepts in the dormant stage are the “membrane or protection layer concept” and the concept of “delayed nucleation and growth” (Breugel, 1997; Guang, 2003).

2.1.2.3 Acceleration stage (Stage III)

At the end of the dormant period, the alite (C_3S) and belite (C_2S) in the cement start to hydrate, with the formation of calcium silicate hydrate and calcium hydroxide (Equations 3 and 4). This corresponds to the main period of cement hydration known as the acceleration stage during which time cement product strength increases. The C_3S and belite C_2S cement grains react from the surface inwards, and the anhydrous particles become smaller through a gradually thickening shell (Breugel, 1997). C_3A hydration also continues, as fresh crystals become accessible to water (Eqn. 2.1).

The period of maximum heat evolution occurs typically between about 10 and 20 hours after mixing and then gradually tails off. In a mix containing Portland cement as the only cementitious material, most of the strength gain occurs within about a month. Ferrite hydration also starts quickly as water is added, but then slows down, probably because a layer of iron hydroxide gel forms, coating the ferrite and acting as a barrier, preventing further reaction (Eqn. 2.5).

2.1.2.4 Post-acceleration stage (Stage IV)

The rate of heat liberation slows down (stage IV) after peaking in Stage III. The hydration of C_2S becomes the main contribution to this stage. Richardson *et al* (1989)

suggested that it is also due to the conversion of calcium alumina ferric oxide tri-sulphate hydrates (AFt) to alumina ferric oxide mono-sulphate hydrates (AFm) and the formation of secondary AFt. The main products in this stage are $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ (AFm).

2.1.3 Thermal Analysis of Portland cement

Cement undergoes phase changes when it is subjected to heat treatment between 20°C and 1100°C . The reactions that occur with an increase of temperature in cement paste and concrete according to Lea (1970) and Sharma and Pandey (1999) are summarized as follows:

- From 30°C to 105°C ; surface water begins to evaporate and a part of the bound water escapes. It is generally considered that the evaporable water is completely eliminated at 120°C .
- Between 110°C and 170°C : the decomposition of gypsum (with a double endothermal reaction) and ettringite occurs and the loss of water from part of the carboaluminate hydrates takes place.
- Between 180°C and 500°C : the loss of bound water from the decomposition of the C-S-H and carboaluminate hydrates occurs and
- From 450°C to 550°C : dehydroxylation of the portlandite (calcium hydroxide) takes place.
- $700\text{--}900^\circ\text{C}$: decomposition of calcium carbonate.

2.2 Limestone

Limestone is a sedimentary rock that is composed primarily of CaCO_3 . It forms from both the chemical precipitation of calcium carbonate and the transformation of shell, coral and algal debris into calcite during diagenesis over several thousand years. Limestone is also formed as a deposit from the precipitation of calcium carbonate. Marble is a metamorphic rock that forms when limestone is subjected to heat and pressure. If it contains more than 95% of calcium carbonate it is referred to as high-calcium limestone or calcite (Boynton, 1980). When a considerable part of the calcium molecules is replaced by magnesium, it is known as magnesium limestone or dolomite limestone.

The physical and chemical properties of a typical limestone are presented in Table 2.1 (Boynton, 1980; Kesse 1985). It gives a hardness of 3 – 4 on the Moh's scale and has a density of between 1800 and 2100 kg/mm^3 . Chemically, it is composed mainly of CaO (38% - 42%), and SiO_2 (20% -25%).

2.2.1 Portland Limestone Cement (PLC)

Limestone is an important material for cement manufacture. The addition of limestone to Portland cement significantly improves several cement properties such as compressive strength, water demand, workability and durability. The addition of limestone increases the hydration rate of the clinker minerals.

Table 2.1: Properties of a typical limestone (Boynton, 1980)

Physical properties	Value
Hardness, Moh's scale	3 – 4
Bulk density, kg/mm ³	2000 – 2800
Specific gravity	2.5 - 2.9
Compressive strength, N/mm ²	20 – 195
Shear strength, N/mm ²	4 – 20
Water absorption, %	< 1.0
Porosity, %	0.3 – 12
Weather Impact	Resistant
Chemical properties	
Lime (CaO) , %	38-42
Silica (SiO ₂) , %	20-25
Alumina (Al ₂ O ₃), %	2-4
Other Oxides like Na, Mg, %	1.5 to 2.5
Loss On Ignition, %	30-32

Several research studies have shown that limestone filler acts both as inert and active additive in the hydration of cement. It has been proven that there is interaction between calcium silicate and calcium carbonate (CaCO₃) and that calcium carboaluminate hydrates precipitate during hydration of cement containing CaCO₃ (Sprung and Siebel, 1990; Neto and Campiteli, 1990; Livesey, 1991; Bertrand and Poitevin, 1991; Cochet and Sorrentino, 1993; Pèraet *al*, 1999). The presence of limestone in Portland cement influences the rate and degree of cement hydration as well as the phase composition of hydrated cement paste. The addition of limestone increases the hydration rate of clinker minerals (3CaO.SiO₂ and 2CaO.SiO₂). The acceleratory effect is more

pronounced with increased content and greater fineness of limestone. The formation of ettringite is also enhanced but its tendency to transform to monosulphate is diminished (Klieger and Hooton, 1990; Hawkins, *et al* 2003). The monosulphate is further converted into a more stable monocarboaluminate; the remaining monosulphate reacts with the liberated SO_4^{2-} anions and ettringite is formed. Calcium silicate hydrate can include CO_3^{2-} anions in its structure and, consequently, calcium silicocarbonate hydrates form. Calcium carboaluminate hydrates usually form in cements that are rich in 3CaO ; Al_2O_3 . (Pèra *et al*, 1999; Sharma and Pandey, 1999; Catinaud, *et al* 2000; Kakaliet *al* 2000; Bonavettiet *al*, 2001; Rahhal and Talero, 2005).

2.2.2 The effect of limestone addition on C_3A hydration

The presence of ground limestone affects the hydration of Portland cement. Kakaliet *al*. (2000) found that CaCO_3 suppresses the conversion of Alumina Ferric oxide trisulphate (Aft) to Alumina Ferric oxide monosulphate (AFm) and reacts with C_3A to produce monocarbonate hydrate from the beginning in the $\text{C}_3\text{A} + \text{CaCO}_3$ system. According to Bonavettiet *al* (2001), in the $\text{C}_3\text{A} + \text{CaCO}_3 + \text{Ca}(\text{OH})_2 + \text{H}_2\text{O}$ system, the phases of calcium tricaboaluminate and calcium hemicarboaluminate are observed, but no calcium tricaboaluminate is formed. In the $\text{C}_3\text{A} + \text{CaCO}_3 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CH} + \text{H}_2\text{O}$ system, Aft, AFm, calcium monocarboaluminate and calcium hemicarbonate hydroxide are the hydration products. Zhang and Zhang (2008) blended pure C_3A with 40% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Sample A), 8% CaCO_3 + 32% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Sample B), 24% CaCO_3 + 16% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Sample C) and 40% CaCO_3 (Sample D). The isothermal

calorimetry curves showing the rate of heat development of pure C_3A blended with limestone are presented in Fig. 2.3.

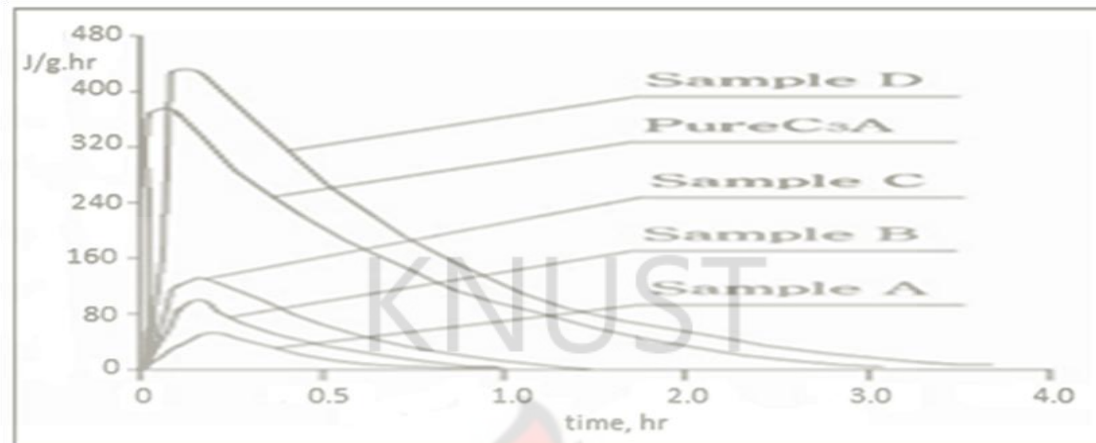
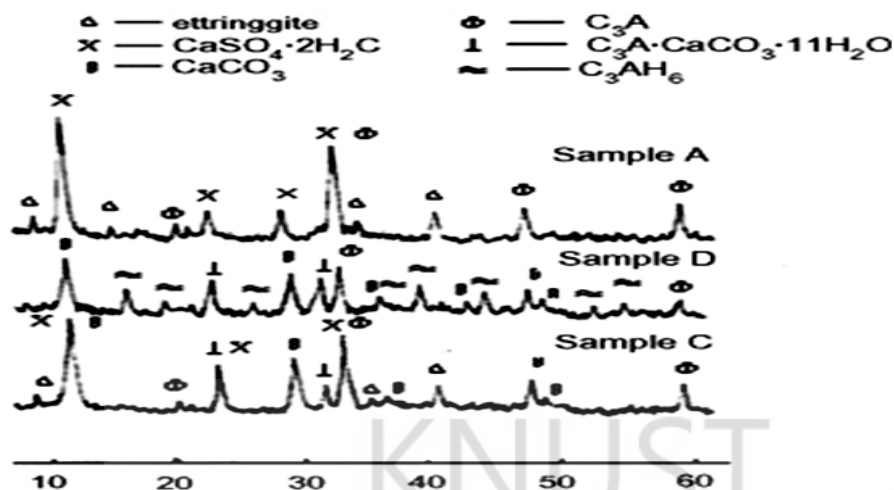


Figure 2.2: Rate of heat development of C_3A - $CaCO_3$ - $CaSO_4 \cdot 2H_2O$ paste (Zhang and Zhang, 2008)

The maximum peaks of heat development and total heat resulting from samples A, B and C were lower than that of pure C_3A , with sample A giving the lowest value. However, values obtained for sample D were higher than those of C_3A sample. The result indicated that hydration of C_3A was greatly stayed by gypsum $CaSO_4 \cdot 2H_2O$, while $CaCO_3$ accelerated the hydration of C_3A . It therefore showed that $CaCO_3$ was an active player during hydration. However, the hydration was controlled when $CaSO_4 \cdot 2H_2O$ and $CaCO_3$ coexist. As shown in Fig. 2.4, there was only ettringite in the paste of sample A. In the paste of sample D, there were calcium aluminate oxide hydrate $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and calcium aluminate monocarbonate $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$. There were ettringite and $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ as products of sample C but $3CaO \cdot Al_2O_3 \cdot 6H_2O$ was not.



20

Figure 2.3: XRD patterns of $C_3A-CaCO_3-CaSO_4 \cdot 2H_2O$ pastes hydrated for 1day (Zhang andZhang, 2008)

2.2.3 The effect of limestone addition on C_3S hydration

Addition of $CaCO_3$ accelerates the hydration of C_3S and results in the formation of calcium carboxysilicate hydrate (Peraet *al.* 1999; Kakaliet *al.*, 2000). Figure 2.5 presents the isothermal calorimetry curves showing the rate of heat development of pure C_3S blended with limestone powder at 5% (E), 10% (F) and 15% (G) (Zhang and Zhang, 2008).

Isothermal calorimeter curves (figure 2.6) show that the rate of the heat evolution of a blended system is always higher than that of pure C_3S system according to Zhang and Zhang (2008). The X-ray diffraction (XRD) study shows that the formation of calcium carboxysilicate hydrate starts after 60 days. The above observations indicate that $CaCO_3$ not only modifies the hydration of C_3S , but also reacts with it to form calcium carboxysilicate hydrate.

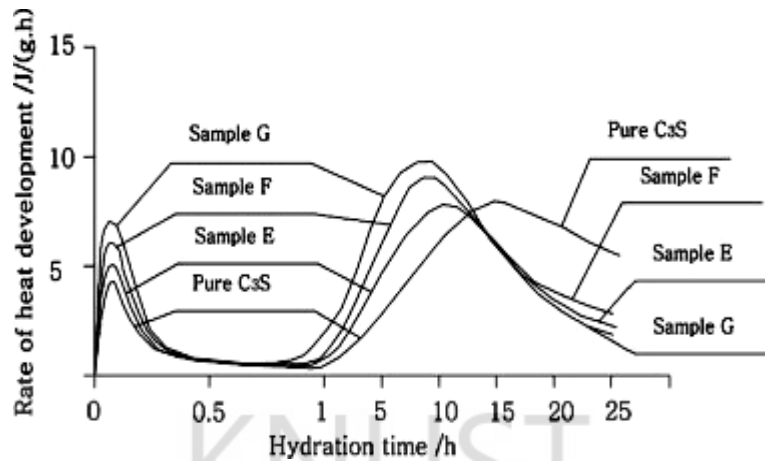


Figure 2.4: Typical heat evolution curves of Portland cement blended with limestone (Zhang and Zhang, 2008)

It shows that higher rates of heat development were obtained with higher CaCO_3 levels. The total heat resulting from pure C_3S was much less than that of blend samples by 15 hours. This means CaCO_3 cannot be considered as an inert addition when C_3S hydrates. It rather takes part in the hydration process.

2.2.4 Microstructure of Portland cement blended with Limestone

Apart from hydration acceleration of Portland clinker grains (especially the C_3S) at early ages, addition of milled limestone improves the particle packing of the cementitious system. It also provides new nucleation sites for formation of larger size of calcium hydroxide at early stage, and produces the formation of calcium carboaluminates as a result of the reaction between CaCO_3 from limestone and C_3A from Portland clinker (Soroka and Setter, 1977; Ramachandran, 1984; Cochet and Sorrentino, 1993). Fig. 2.6 shows the XRD patterns corresponding to the plain cement and limestone cement pastes. For the plain cement, the hydration products at one day were ettringite and calcium hydroxide from silicate hydration reactions. In the XRD pattern at 3 days, the

ettringite conversion to monosulphoaluminate was detected. This conversion implied a progressive increase of the monosulphoaluminate peak up to 90 days.

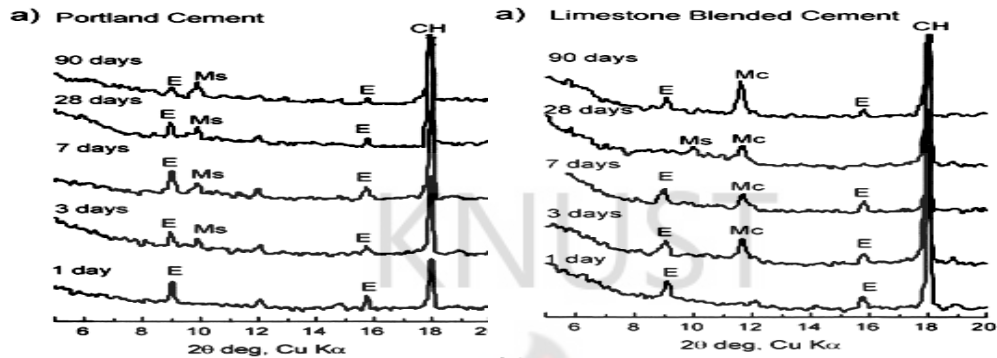


Figure 2.5: XRD patterns of hydrated Portland and blended limestone cement pastes (Soroka and Setter, 1977)

E=ettringite, Ms=monosulphoaluminate, Mc=monocarboaluminate and CH=calcium carbonate

This conversion implied a progressive increase of the monosulphoaluminate peak up to 90 days. Several XRD studies (Barker and Cory, 1991; Pèra, *et al*, 1999; Bonavettiet *al*, 2001; Voglis *et al*, 2005) indicated the formation of monocarboaluminate and calcium carbosilicate hydrate in the PC paste blended with limestone.

2.2.5 Properties of Portland Limestone Cement (PLC)

Several research works and experiments by reputable researchers the world over have adequately shown that PLC is a durable and good cement that can be used for all types of concrete construction works in both tropical and temperate regions. This cement has been used in Europe, especially France and Germany, since 1980 for all types of construction without any adverse effect (Pera *et al*, 1999). Portland limestone cement

was introduced in Ghana in 2003 and has been the predominant type of cement used for construction.

2.2.5.1 Thermo and infrared analysis of cement

Zhang and Zhang(2008) studied the hydration of a C_3S blended with 10% by mass of calcium carbonate using Differential Thermal Analysis (DTA) and infrared analysis. The analyses were run from 28°C to 1000°C with a $10^{\circ}\text{C}/\text{min}$ heating rate and 100 ml/min of air as the purge gas. Figure 2.7 presents the various endothermic peaks of phase changes of the Portland cement, pure CaCO_3 and PLC pastes. It shows that the dehydroxylation of the portlandite (calcium hydroxide) occurred at 487°C for C_3S as compared to 579°C for PLC. This gives the influence of CaCO_3 on cement hydration.

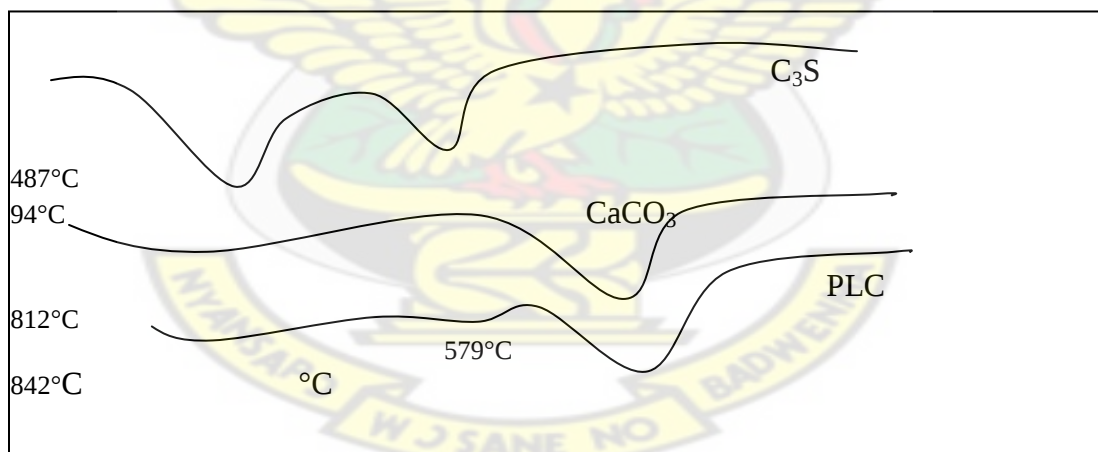


Figure. 2.6: DTA patterns of PLC paste compared with CaCO_3 and C_3S paste at 28 days (Zhang and Zhang, 2008).

The IR spectrum for blended cement (treated sample) was compared with that of CaCO_3 in Fig. 2.8. In the treated sample, all of characteristic bands of CO_3 ion appeared and new wave numbers at 525 cm^{-1} , 760 cm^{-1} , 1160 cm^{-1} , 1250 cm^{-1} , 1460 cm^{-1} ,

1540 cm^{-1} , 1600 cm^{-1} and 1620 cm^{-1} could be observed. That might mean other ions went into the structure of CaCO_3 .

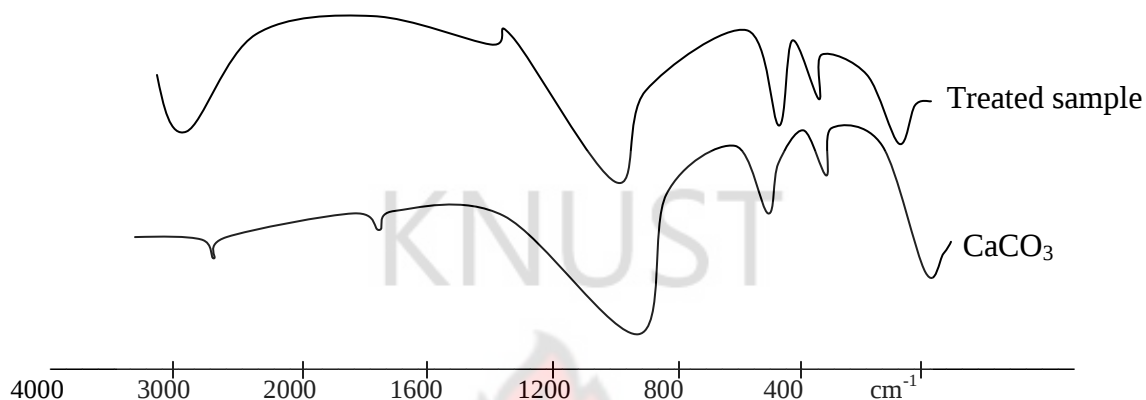


Figure. 2.7: Infrared spectra of PLC (treated sample) paste compared with CaCO_3 at 28 days (Zhang and Zhang, 2008).

2.2.5.2 Physical, Chemical and Mechanical Properties

Work by Tsiviliset *al* (2002) on PLC gave various results of its physical, chemical and mechanical properties. Their study involved the inter-grinding of clinker, limestone and gypsum in a laboratory using a ball mill. The limestone content ranged from 10% to 40%. The properties of the cements and other materials are shown in Tables 2.2- 2.4. The results of Tables 2.3 and 2.4 clearly show that addition of CaCO_3 to cement up to 35% give strengths suitable for general construction and concrete works. CaCO_3 content of 20% gives early higher strength than the reference cement. Even though strengths of the limestone cement concretes were lower than the reference they were above 25N/mm² at 28 days.

Table 2.2: Chemical and mineralogical composition of clinker and limestone used (Tsiviliset *al*, 2002)

Oxide	Chemical Composition (%)		Composition	
	Cement	Limestone	Mineral compound	Cement (%)
SiO ₂	21.96	0.55	C ₃ S	61.59
Al ₂ O ₃	5.15	0.40	C ₂ S	16.48
Fe ₂ O ₃	3.78	0.17	C ₃ A	7.27
CaO	65.95	53.47	C ₄ AF	11.50
MgO	1.76	1.02	Moduli	
K ₂ O	0.56	0.03		
Na ₂ O	0.12	0.01	LSF	94.20
SO ₃	0.52	-	SR	2.46
LOI*	-	43.13	AR	1.36
			HM	2.14

*LOI – loss on ignition, LSF –lime saturation factor , SR – silica modulus, AR – alumina modulus, HM –hydraulic factor

Table 2.3: Properties of Portland limestone cement mortar (Tsiviliset *al*,2002)

Sample	Limestone Content, %	Specific surface, (cm ² /g)	Compressive Strength, N/mm ²			
			1 day	2 days	7 days	28 days
C	0	2600	11.9	21.3	35.3	51.1
PLC1	10	3400	11.2	20.9	36.3	47.9
PLC2	15	3660	12.9	22.7	37.7	48.5
PLC3	20	4700	14.9	24.3	38.1	48.1
PLC4	35	5300	9.8	17	26.2	32.9

C – Reference cement; P LC1..4 – Portland limestone cement

Table 2.4: Properties of Portland limestone cement concretes (Tsiviliset *al*,2002)

Sample	Slump mm	Flow mm	Unit weight kg/m ³	Compressive strength, N/mm ²	
				7 days	28 days
C	130	460	2400	26.7	31.9
PLC1	120	440	2395	21.9	27.4
PLC2	120	420	2400	22.5	27.3
PLC3	110	420	2394	22.1	28.0
PLC4	110	400	2390	21.6	26.6

C – Reference cement; P LC1..4 –Portland limestone cement

2.3 Clam shells

Clam shells are purer form of CaCO_3 in Ghana than limestone (<49%) containing more than 50% of lime (CaO) on heating above 800°C . They are usually found on river beds as fresh type of shell fish or empty shells after thousand years of accumulation (Kesse, 1985). Table 2.5 shows clam shells found in Ghana and their average chemical composition respectively.

Table 2.5: Average Chemical Analysis of Clam Shells (Atiemo, 1997)

Chemical Composition	Clam Shells, wt%
CaO	53.4
SiO ₂	2.1
Fe ₂ O ₃	0.5
Al ₂ O ₃	0.3
MgO	0.6
Loss on ignition	43.4

2.3.1 Properties of Clam shell-filled cement

Atiemo (1997) studied the suitability of clam shells as filler in Class 32.5 ordinary Portland cement for masonry works. The masonry cement was prepared by first blending ordinary Portland cement with the ground clam shells. The percentage by mass of the filler in the masonry cement varied from 10% to 40%. The study was carried out on 1:3 and 1:5 cement to sand mortar mixes as stipulated by EN 196-2 and BS 4551 respectively. Table 2.6 gives the mortar mix designs whilst results of the compressive strength tests of the composite and masonry cements containing 10%-40% by mass of ground clam shells are given in Table 2.7. Each strength value represents an average of 5 cubes.

The 28-day compressive strength of the masonry cement with up to 25% filler content was higher than the minimum standard value of 3.6N/mm^2 for type (iii) mortar stipulated by BS:5628-2. It is also observed that the compressive strength of the mortar cubes increased in all cases with time. The compressive strengths of the 1:5 mortars with 10% filler content were higher than that of the control at all times. This is attributed to the accelerated rate of hydration with the filler serving as the crystallization nuclei (Soroka and Setter 1977). The strength, however, decreased with increased percentage of filler content, always below that of the control. This is expected because the excess filler material rather acted as a dilutant thus affecting the strength of the mortar eventually. Fig. 2.9 gives the 28-day compressive strengths of the masonry cement with up to 40% clam shells content as compared to the minimum strength of 3.6N/mm^2 .

Table 2.6: Mix design of cement mortar mixes (Atiemo, 1997, 1998)

Specimen	Cement, g	Clam shells, g	Sand, g	Water:binder ratio
Control (C)	300	-	900	0.4
M1	270	30	900	0.4
M2	240	60	900	0.4
MS1	180	20	1000	0.9
MS2	160	40	1000	0.9

M1,M2,MS1,MS2 – blended cement containing clam shells; C – reference cement

Table 2.7: Compressive strengths of clam shell cement mortar mixes (Atiemo, 1997, 1998)

Sample	CaCO ₃ Content, %	mortar mix	Compressive Strength N/mm ²			
			3days	7 days	28 days	42 days
M0	0	1:3	8.7	20.5	31.6	39.4
M1	10	"	8.6	19.8	31.3	38.7
M2	20	"	7.6	16.5	22.4	28.4
M3	25	"	7.1	12.3	19.6	25.7
M4	30	"	5.9	9.0	17.8	23.9
M5	40	"	4.5	7.8	12.5	18.7
MS0	0	1:5	2.8	3.0	7.0	10.6
MS1	10	"	3.0	3.2	7.2	11.8
MS2	20	"	2.7	2.9	5.2	8.3
MS3	25	"	2.1	2.3	4.2	6.8
MS4	30	"	2.1	2.1	3.1	5.9
MS5	40	"	1.0	1.2	2.2	4.3

M0,MS0 = OPC; M1 ... M.5,MS1 MS5= blended cement containing clam shell

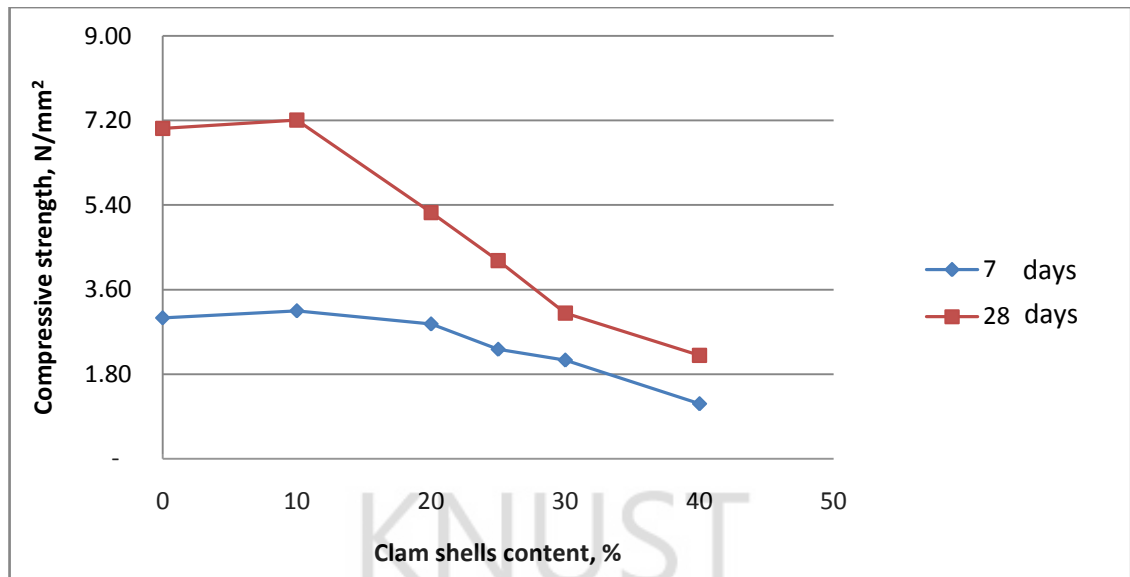


Figure 2.8: Compressive strength of 1:5 cement mortars containing clam shells

It is noted from the graph that the 28-day compressive strengths of the masonry cement mortar cubes containing up to 25% clam shells filler produced strengths above 3.6 N/mm^2 as specified for type (iii) mortars and plasters (BS 4551).

From the various tests and analysis, it has been shown that ground clam shells can be used as filler up to 25% by mass for the production of masonry cement. The 28-day compressive strength of mortar cubes of the masonry cement containing up to 25% of ground clam shells as filler was higher than the standard value of 3.6 N/mm^2 . Therefore, the masonry cement can be used to bond and render hollow and solid sandcrete blocks for housing construction.

2.4 Steel Slag

Steel slag (SS) is an industrial waste resulting from the steel-refining process in a conversion furnace. An estimated fifty million (50) tonnes steel slag are produced in the world and nearly 12 million tons in Europe annually as residue. Owing to the

intensive research work in the past 30 years, about 60% of the steel slag is currently used in fields of technological application. The remaining 35% of these slags are still dumped as waste (Wu *et al*, 1999; Tsakiridis *et al*, 2008).

In Ghana, steel slag waste is produced by four main steel companies; namely, Western Casting and Forming Company, Wahome Steel Works, Tema Steel Works and Ferro Fabric Co. Ltd., all based in Tema. An estimated 5,000 tonnes of slag are dumped as waste every year for the past 20 years.

The chemical composition of a typical steel slag is given in Table 2.8. It consists mainly of calcium oxide, iron oxide, silica and aluminium oxide, which constitute more than 70% of the material.

Table 2.8: Chemical composition of a typical steel slag (Tsakiridis *et al*, 2008)

Chemical compound	Percentage, %
CaO	45–60
SiO ₂	10–15
Al ₂ O ₃	1–5
Fe ₂ O ₃	3–9
FeO	7–20
MgO	3–13
P ₂ O ₅	4

The common mineral compositions of steel slag, among others, include C₃S, C₂S, C₄AF, C₂F, RO phase (a solid solution of MgO, FeO, and MnO), olivine and free lime (Tsakiridis *et al*, 2008). Steel Slag could be classified into four groups such as

the olivine group, merwinite group ($A = 1.4-6$), dicalcium silicate group ($A=1.6-2.4$), and tricalcium silicate group ($A = 2.4$); where A (Alkalinity) is calculated as:

$$A = \frac{CaO + MgO + Al_2O_3}{SiO_2} \quad 2.7$$

The presence of C_3S , C_2S , C_4AF and C_2F generates the cementitious properties of steel slag. However, the C_3S content in steel slag is much lower than in Portland cement. Slag cement also contains amorphous silica (S) which reacts with calcium hydroxide (CH) to form additional C-S-H thereby improving strength (Eqn. 2.8).



Slag cement is not only pozzolanic but is also hydraulic, meaning the slag cement will hydrate when mixed with water (Hale *et al*, 2008).

Thus, steel slag can be regarded as a weak Portland cement clinker and can be used as partial substitution for clinker to produce composite Portland cement (CPC). Steel slag cement can be used for general construction purposes, and it is especially suitable for mass concrete and pavement applications due to its special features. This type of cement has the advantages of lower energy cost, higher abrasion resistance, lower hydration heat evolution and higher latter strength development. Its usage also reduces greenhouse and noxious gases such as CO_2 , SO_2 , NO_x etc because of replacement of clinker. Furthermore, steel slag is used as asphalt concrete aggregate in some countries (Daimon, 1980; Mehta, P.K., 1981; Tüfekçi *et al* 1997; Dongueet *al* 1997; Tsakiridis *et al*, 2008). Studies by Tüfekçi (1997) show that the

mineralogical phases of a typical steel slag produced by steel plants, and determined by X-ray diffraction (XRD) are belite, alite, ferrite, wustite, quartz, periclase, (Fig. 2.10).

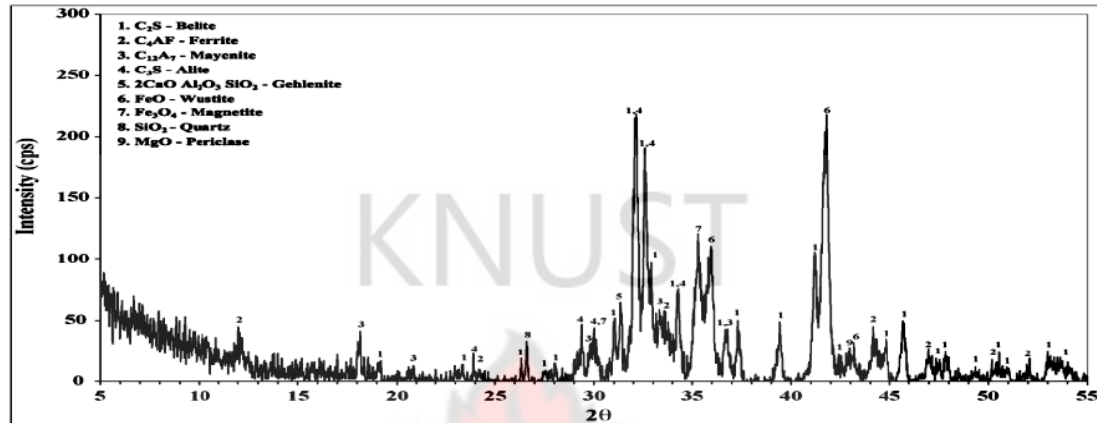


Fig. 2.9: X-ray diffraction of a typical steel slag (Tüfekçiet *al*, 1997)

The main problem with using steel slag in civil engineering works is the possible presence of free lime, especially large-sized components of heated undissolved limestone. When the free lime hydrates it is converted to $\text{Ca}(\text{OH})_2$, its volume increases causing swelling so its presence in cement affects the quality of concretes. However, steel slag cement, which is composed mainly of steel slag, blast furnace slag and cement minerals (C_3S , C_2S etc.), has been commercially produced and marketed in China for more than 20 years. It uses approximately 40% of the total steel slag production in China. Blended cements comprising mainly of OPC with mixture components of slag and other admixtures as cheap raw materials have gained recognition for low porosity which imparts high ultimate compressive strength (Tüfekçiet *al* 1997; Dongueet *al* 1997).

Steel slag cement has the disadvantage of longer setting time and lower early strength when compared with ordinary Portland cement. But these are compensated by the addition of other admixtures and usage of high-strength cement or high quality clinker and higher fineness.

Today, most metallurgical steel slags are used as aggregates for different applications, and only the ground granulated blast furnace slag is used for a partial Portland cement replacement. It also improves the microstructure and durability of hardened Portland cement and concrete very significantly. Existing literature has given little attention to the use of steel slag in combination with other admixtures like pozzolana and clam shells in the raw meal for the production of Portland cement.

2.4.1 Properties of Steel Slag Cement

2.4.1.1 Hydration of steel slag cement

The hydration of steel slag is basically the dissolution of the silicate chain structure and aluminate in the slag by hydroxyl attack. For the slag to continue hydrating, Ca^{2+} and OH^- from the slag are not enough, so an external supply becomes necessary. In low water/cement concrete, the supply of external OH^- is drastically diminished. The elution of selective ions is therefore delayed; the reaction rim only begins to be visible from the seventh day of hydration. Ettringite crystal formation in the early stages of ordinary slag hydration in concrete acts as a binder, resulting in the higher strength. A number of researchers have observed ettringite (AFt) rods on slag particles during their initial hydration. In concrete with low lime slag, ettringite may be lower (Daimon, 1980; Mehta, 1981; Cook *et al*, 1987; Kourounis *et al*, 2007).

Kourouniset *al* (2007) studied the hydration products of steel slag cements mineralogically by x-ray diffraction. The cement pastes were cured in tap water at $20 \pm 2^\circ\text{C}$ and observed at 2, 7, 28 and 90 days. Fig. 2.11 shows the X-ray diffraction patterns of cement with 15% steel slag hydrated for 1, 2, 7, 28 and 90 days. It can be seen that the main hydration products were calcium silicate hydrates ($\text{CaSiO}_2 \cdot \text{H}_2\text{OH}$), calcium hydroxide ($\text{Ca}(\text{OH})_2$) and ettringite ($6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) as well as unhydrated C_3S and C_2S . The peaks of the calcium silicates phases diminished, especially at the age of 90 days.

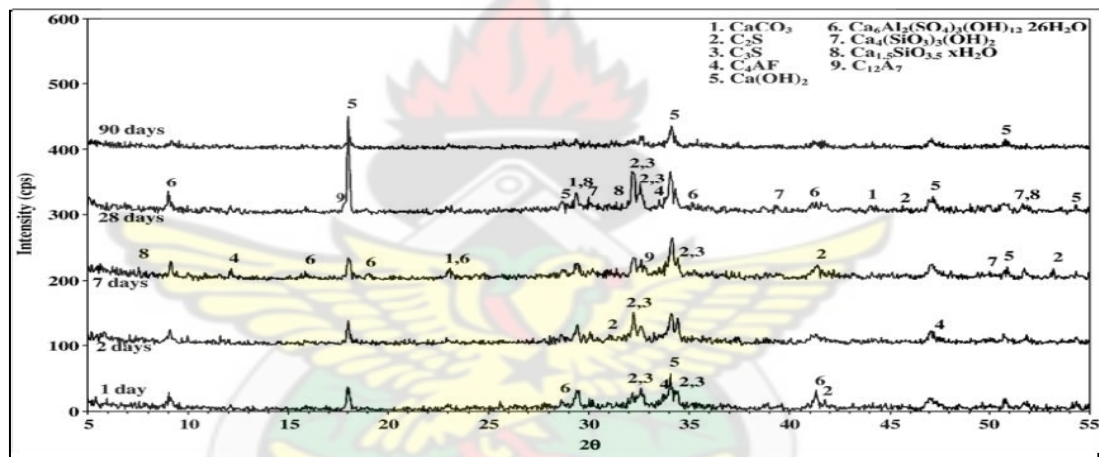


Figure 2.10: X-ray diffraction of cement with 15% steel slag, hydrated at various ages (Kourouniset *al*, 2007).

2.4.2 Microstructure of steel slag cement

The microstructure of the ordinary Portland cement (oPc) clinkers and steel slag cement (SSC) were also examined by optical microscopy in polished sections by Tsakiridis *et al* (2008). The addition of the steel slag by 10.5% did not seem to affect its microstructure and the formation of its characteristic mineralogical phases (Figs. 2.12 and 2.13). Both clinkers contained more or less euhedral alite and they exhibited coalescence of alite crystals. The alite crystals appeared well formed, with average

size $40\mu\text{m}$, whereas no decomposition of C_3S was observed. In the optical microscope, belite was observed as bluish or brownish rounded crystals, rich in lamellas. No differences in the microstructure of belite between Portland cement and steel slag cement clinkers were detected. In both cases, the brownish belite crystals were evenly distributed in relation to alite. Finally, the liquid phase solidified as uniformly distributed fine crystals (Tsakiridis *et al*, 2008).

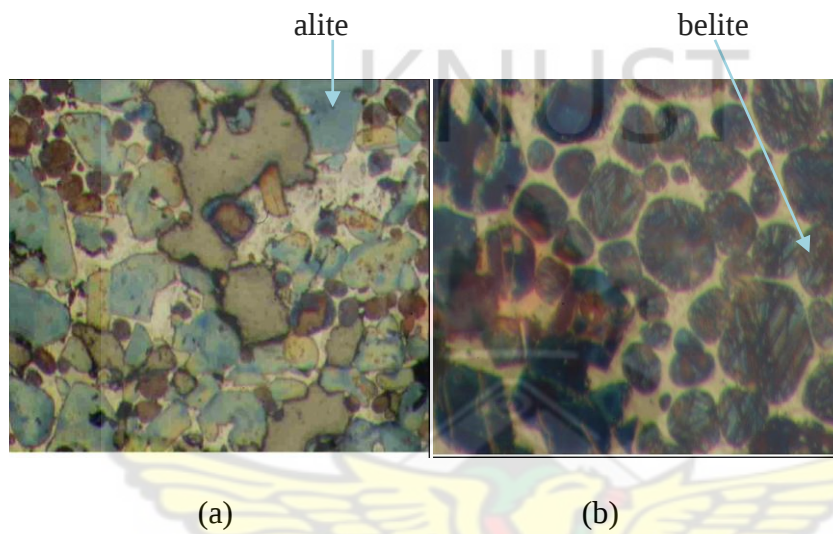


Figure 2.11: Microstructure of Portland cement clinker without steel slag. (a) Large alite crystals (500x). (b) brownish rounded belite crystals (500x).

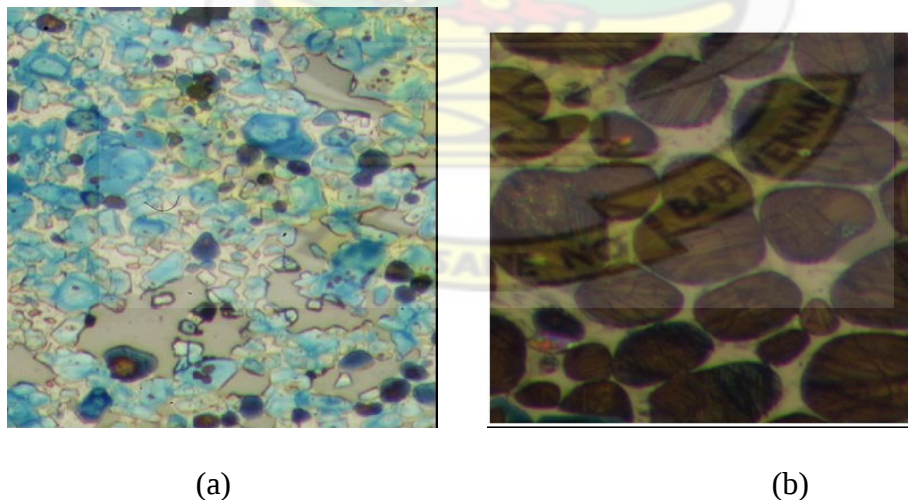


Figure 2.12: Microstructure of Portland cement clinker with steel slag (a) alite crystals (500x). (b) brownish rounded belite crystals (500x) (Tsakiridis *et al*, 2008)].

2.4.3 Physical, Chemical and Mechanical properties of steel slag cement

Tüfekçiet *al* (1997) also undertook a research study on steel slag for cement production. Portland cement (PC) was blended with 5% and 10% of two industrial steel slag samples, named A and B respectively. The chemical compositions of the steel slag samples and their blends with cement are given in Table 2.9. The mechanical properties of the slag cement mortars and pastes are also given in Table 2.10. It shows that the steel slag cement blends required less water than that of the control. Also, both blended cements gave strengths higher than 41.0MPa at 28 days. The results also show that the slag cements initially set slowly comparatively but set finally before the oPc. The setting times of the slag cements were higher than the control but within the standard limits of EN 197-1 (2000).

Table 2.9: Chemical compositions of SS-A and SS-B and their mixtures (Tüfekçiet *al*, 1997)

Material	Composition, %						
	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	SO ₃	LOI*
Control (oPc)	22.82	5.28	5.85	62.95	1.45	1.05	0.60
Steel slag, A	41.39	31.39	3.58	4.22	0.66	0.20	18.46
Steel slag, B	57.48	33.73	2.19	1.53	0.47	0.14	2.39
10%A+ 90%oPc	24.67	6.78	5.63	57.08	1.44	1.04	3.25
5%A + 95%oPc	23.75	6.09	5.75	60.01	1.41	1.03	0.97
10%B + 90%oPc	26.22	8.14	5.49	56.83	1.37	0.95	0.90
5%B + 95%oPc	24.55	6.70	5.67	59.97	1.40	0.98	0.73

*LOI – Loss on ignition

Table 2.10: Results of Cement Mortar Tests (Tüfekçiet *al*, 1997)

Cement Sample	Slag Content %	Compressive strength, MPa			Expansion Mm	Water Demand %	Setting time, Min	
		2day s	7days	28days			Initial	Final
oPc	0	26.2	34.8	45.4	10	100	60	600
Cement A	10	22.9	31.0	41.3	9	98	185	255
Cement B	5	25.5	33.5	44.5	4	96	180	255

The aggregate data and compressive strength test results, performed according to Turkish standard, for concretes compared to the control mix are summarized in Table 2.11. It indicates that the compressive strength of the concrete with cement mix of 10% SS-AI + 90%C increases slowly when compared with 5% SS-B1 + 95% C mortar mix. This is due to the 5% higher replacement of cement by a less reactive material. In all cases, slag b cements performed better than that of slag A.

It shows that slag cements have lower early strength, which is attributable to the slow growth of calcium silicate hydrates gel. In the case of very high-strength concrete, however, this is compensated by the density of the solid body.

The chemical, physical and mechanical properties of slag blended cement were also researched by Wu *et al* (1999). In this case clinker, steel slag (SS), fly ash (FA) and gypsum were ground together to the fineness of 2-4% of the residue on a 0.08mm standard sieve to produce the desired cement. The total amount of SS and FA was 50%, and the amount of SS and FA was fixed at 30 and 20% respectively. The slag contained mainly CaO (48.2%) whilst FA consists of 48.5% silica. The mix compositions for the control cement (C) and blended slag cement with varying quantities of slag, fly ash and gypsum (M1 to M4) as well as the mechanical

properties are shown in Table 2.12. The results obtained showed that all the specimens of slag blended cement could reach the required strength grade of 42.5N. The flexural strengths for the control and blended cements were almost the same as the control. The setting time was, however, relatively long for the requirement of construction work, which may be related to the low-alumina content (2.58%) of steel slag. The results showed that the admixtures gave strengths that satisfy standard specifications for Class 42.5N cement (EN 197-1).

The afore-mentioned extensive studies really show that steel slag has the potential as ingredient in cement production in Ghana; it is already being utilized in China and other countries as pozzolana. This makes a serious case for the evaluation of steel slag waste obtained in Ghana for cement production and usage for construction. The added advantages include reducing cost of cement, elimination of environmental degradation and greenhouse effects. About 5000 tonnes of steel slag waste are produced annually in Ghana.

2.5 Clay Pozzolana

Pozzolanas are defined as siliceous and aluminous substances which are by themselves not cementitious but in their finely-divided form react with lime in the presence of water at ordinary temperature to produce hydraulic compounds. They occur naturally or are produced artificially. Natural pozzolanas are materials which in their natural state and finely-divided form react with lime to produce hydraulic compounds. They are mainly produced from volcanic matter and are described as incoherent pyroclastic materials.

Table 2.11: Test Results for Concretes from Cement and Slag Mixtures (Tüfekçiet *al*, 1997)

Cement	Materials (g)				Water	Expansion mm	Compressive strength (MPa)			
	Slag A	Slag B	Sand	Crushed stone			1 day	7 days	28 days	56 days
410	0	0	1215	1540	260	10.7	26.3	32.9	35.6	38.7
390	21	-	1210	1520	250	8.9	19.1	26.7	28.0	30.5
370	42	-	1210	1530	240	7.9	22.1	28.7	30.0	34.5
350	60	-	1212	1520	232	7.3	19.1	26.7	28.6	30.9
390	-	21	1213	1522	245	9.9	25.2	31.7	34.9	37.6
370	-	42	1210	1525	235	9.7	24.8	30.9	33.7	37.0
350	-	60	1212	1530	225	9.4	24.2	30.1	32.8	36.7

Table 2.12: Properties of slag blended cement mortar (Wu *et al*, 1999)

Specimen	Clinker	Steel slag	Fly Ash	Gypsum	Setting time, Min		Compressive strength MPa			Flexural strength		
					Initial	final	3days	7 days	28 days	3 days	7 days	28 days
Control	93	-	-	7	100	145	23.4	39.6	51.6	4.7	7.0	8.4
M1	47	30	20	3	285	366	20.5	27.5	43.8	4.3	5.8	7.4
M2	46	30	20	4	254	333	21.4	29.0	44.2	4.3	5.9	8.1
M3	45	30	20	5	206	359	20.8	28.5	44.7	4.4	5.7	8.0
M4	44	30	20	6	193	293	20.8	28.5	45.9	4.4	5.9	8.2

The chemical compositions of the natural Italian pozzolanas are related to that of magma. Examples are Italian pozzuolli, tuff, trass, pumicite and diatomaceous earth (Lea, 1970). Artificial pozzolanas are materials that have to undergo heat treatment before they become pozzolanic. Examples are clays, fly ash, blast furnace slag, bauxite waste, shales and spent oil.

2.5.1 Clays and Clay Minerals

Clay is defined as a fine-grained earthy material which contains clay minerals and is plastic and cohesive (Ayetey, 1977; BS.1377:1990). Clays differ mineralogically and chemically, and consequently in their physical properties. They shrink when dry and expand when wet and show gains in strength with retention of shape on firing.

Clay minerals are very tiny crystalline substances that are evolved primarily from chemical weathering of certain rock-forming minerals. Chemically, they are made up of hydrous alumino-silicates and other metallic ions. They are either the two-layer sheet (kaolinite) or the three-layer sheet (montmorillonite) in which silicon and aluminium ions have tetrahedral coordination with respect to oxygen while aluminium, magnesium, iron ions and other ions have octahedral coordination with oxygen or hydroxyl ions as shown in Figs 2.14 and 2.15 (Grim, 1962; Holtz and Kovacs, 1981)

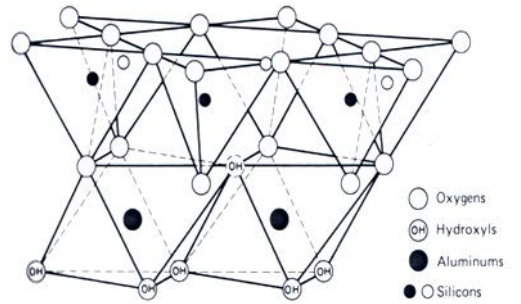


Figure 2.13: Atomic structure of kaolinite (Holtz and Kovacs, 1981)

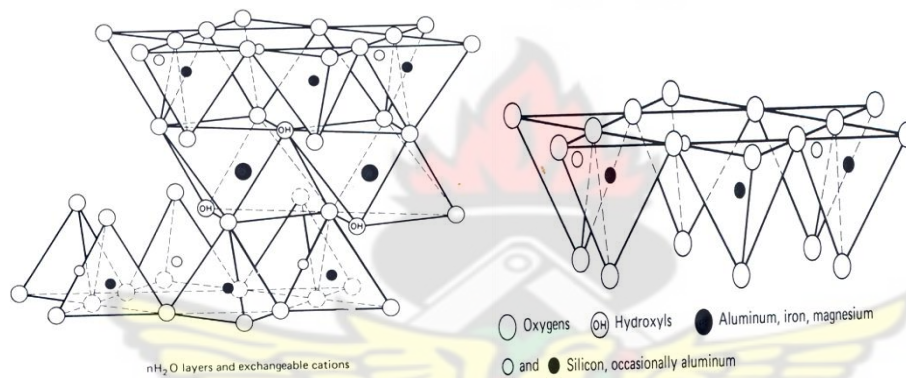


Figure 2.14: Atomic structure of montmorillonite (Holtz and Kovacs, 1981)

All clay minerals are very small, colloidal-sized crystals (diameter less than 2 μm), and they can only be seen with an electron microscope. The particular way in which these sheets are stacked, together with different bonding and different metallic ions in the crystal lattice, constitute the different clay minerals.

Table 2.13 presents the physical and chemical composition of three samples of clay in Ghana (Atiemo, 2005). It shows that the clay samples contain mainly silica (>60%). The clay contents, with particle size of <2 μm , range between 27% and 39.0%.

The pozzolanic activity of clays depends on the type of clay minerals present in the clay which in turn control the chemical composition (Millienzet *al*, 1949). The crystalline clay minerals in their natural state are stable, non-reactive and thus non-pozzolanic. However, imperfections in the crystal structure due to disorderliness and huge internal strains lead to high reactivity. This desirable condition is achieved by calcining and milling the clay beyond 600°C (Uppal and Singh, 1964).

Table 2.13: Properties of three clay deposits in Ghana (Atiemo, 2005)

Property	Mankranso	Mfensi	Bibiani
Physical			
Specific gravity	2.58	2.64	2.58
Plastic limit, %	42.80	43.50	44.45
Liquid limit, %	75.00	78.00	24.48
Plasticity Index, %	37.2	34.5	20
Clay, %	36.0	39.0	27.1
Silt, %	35.0	32.0	52.6
Sand, %	29.0	31.0	20.3
Chemical			
SiO ₂ , %	69.8	60.3	67.6
Al ₂ O ₃ , %	15.70	18.2	16.3
Fe ₂ O ₃ , %	4.60	9.1	4.4
CaO, %	0.20	1.2	0.7
MgO, %	0.10	-	0.1
SO ₃ , %	0.02	0.1	0.04
Loss on ignition	5.30	4.5	4.8

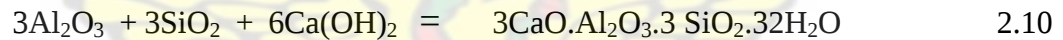
2.5.2 Calcination of Clays and Pozzolannic Activity

Calcination of clays is an important process in the development of satisfactory pozzolanic properties. The pozzolanic reactivity is induced by the destruction of the clay minerals: kaolinite $[\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4]$, montmorillonite $[\text{Al}_2(\text{OH})_2\text{Si}_4\text{O}_{10}]\cdot n\text{H}_2\text{O}$, and illite $\text{K}_2\text{O}_3\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2\cdot 3\text{H}_2\text{O}$. On heating, clay first loses free water at 100°C - 150°C , and from 150°C to 500°C it further loses water that is adsorbed on or between lattice planes of the lattice structure. Disintegration of the lattice structure occurs between 550°C and 650°C with the liberation of H^+ and OH^- ions producing amorphous aluminous and siliceous compound called meta-kaolinite. All these reactions are endothermic. The rate of loss of water becomes high as the temperature rises to 650°C . Dehydration is complete at 750°C (Nutting, 1943; Millien *et al*, 1949, Uppaland Singh, 1964).

The structure is completely disrupted between 800°C - 980°C . Between 940°C and 980°C an exothermic reaction occurs. Mullite ($2\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2$) appears at around 950°C for kaolinite, 1050°C for montmorillonite and 1100°C for illites. The optimum calcination temperature for kaolinitic and montmorillonitic clays for maximum pozzolanic reactivity is between 600°C and 800°C , and 900°C for illites (Millien *et al*, 1949, IS:1344). Kaolinite loses more than 14% of its mass on complete calcination whilst typical montmorillonites and illites lose 5 and 10% of their mass respectively. When the crystalline structure of the clay is ruptured they release siliceous and aluminous compounds and become very unstable and chemically active.

2.5.3 Clay Pozzolanic Action

During hydration of cement, hydrated silicates formed remain stable in contact with lime solution and in the presence of water undergo hydrolysis liberating more lime into the solution (Lea, 1970). The silicate compositions of cement minerals contribute mainly to the structural and strength properties of cement products. They form about 70% of the bulk of cement. The presence of pozzolana active components reduce the amount of free Ca(OH)_2 in cement products considerably. The unstable but reactive siliceous and aluminous compounds of the calcined clay react chemically with the lime producing mostly hydrated silicates of low solubility as given in a simplified form in Equations 2.9 and 2.10.



The products from the pozzolanic reaction add up to the strength of cement products and enhance water-tightness. Extensive studies as well as X-ray diffraction evidence show that pozzolanic reactions are by direct combination of lime and the pozzolana compounds and not by ion exchange (Lea, 1970). Studies on the effect of alumina in pozzolana proved that the presence of alumina in the pozzolana enhances the strength properties of pozzolana cement, particularly during brief curing (Murakami, 1952). They react with lime to form compounds which are very complex. The effects of iron oxide in clay pozzolana were also studied by other researchers. Comparing two clay types which were montmorillonite, Gipps and Britton (1960) observed that the red and yellow clays which contained large amounts of free Fe_2O_3 were more pozzolanically reactive than the black cotton soils, which

did not have free Fe_2O_3 , even though the black soils contain more clay minerals and have higher silica content.

2.5.4 Mechanical Properties of clay Pozzolana cement

Studies on the pozzolanic activity of some clay samples in Ghana for housing construction have been carried out recently in Ghana (Atiemo, 2005; Momade and Atiemo, 2004). Some of the results are presented in Table 2.14. The studies showed that pozzolana cements absorb more water in the preparation of the paste as compared to ordinary Portland cement and the water demand increased in all cases as the replacement of cement was increased. However, the setting times (initial and final) of the pozzolana cements were lower than that of ordinary Portland cement and decrease with increasing amount of pozzolana.

The results also showed that the 28-day compressive strengths of the pozzolana cement mortars up to 30% pozzolana content satisfied the class 32.5 cement as recommended by EN 197-1 (2000) for concrete works and general construction. The Mfensi samples gave the highest strength values in all cases. Generally, the strengths reduce with increasing amount of pozzolana. The study concluded that the clay pozzolana cements are suitable for both concrete and general construction with 25 -30% clay pozzolana content.

Wild *et al* (1997) also reported on pozzolanic properties of selected burnt brick samples produced from clays from four European countries. Clay bricks are burnt at between $800\pm 8^\circ\text{C}$ and 900°C . The bricks were ground in a ball mill and the brick powder samples

were used as partial cement replacement materials (at replacement levels of 10%, 20%, 30% by mass) to prepare mortars. The water/binder (w/b) ratio of 0.4 and the sand to binder (cement plus ground brick) ratio was kept constant at 2.5:1. The average values of compressive strength together with the standard deviations are reported in Table 2.15. The values obtained at 20% were comparable to that of oPc (control).

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Table 2.14: Mechanical properties of pozzolana cement mortar (Momade and Atiemo, 2004)

Sample	Cement Content, %	Pozzolana Content, %	Water, Demand, %	Setting time, min		Water Absorption,%	Compressive strength, N/mm ²		
				Initial	Final		3 days	7 days	28 days
Control	100	0	36.9	108	275	2.1	24.9	36.8	40.2
Bibiani	80	20	37.5	98	265	2.3	21.8	35.2	38.8
	75	25	39.0	92	225	2.1	19.5	31.8	35.6
	70	30	-	-	-	2.1	16.9	25.3	33.5
	60	40	-	-	-	1.85	12.6	22.6	27.1
Mfensi	80	20	38.2	102	250	2.2	23.6	35.5	39.8
	75	25	39.6	90	210	2.2	22.6	33.3	36.8
	70	30	-	-	-	2.0	21.3	27.8	34.1
	60	40	-	-	-	1.8	16.8	23.5	28.8
Wenchi	80	20	38.7	86	241	2.5	22.8	34.1	44.3
	75	25	40.1	75	194	2.3	20.4	31.4	40.8
	70	30	-	-	-	2.2	18.9	28.4	36.8
	60	40	-	-	-	2.4	16.6	24.8	31.3

Table 2.15. Average values of compressive strength for mortar mixes (Wild *et al*, 1997)

Sample	Pozzolana Content, %	Compressive strength, N/mm ²		
		7 days	28 days	90 days
Control	0	51.5 $\pm$ 2.5	60.5 $\pm$ 2.9	65.6 $\pm$ 1.6
Brick B	10	48.3 $\pm$ 2.0	61.6 $\pm$ 2.5	66.3 $\pm$ 3.8
	20	42.8 $\pm$ 4.2	58.3 $\pm$ 3.6	67.5 $\pm$ 2.1
	30	38.4 $\pm$ 2.5	56.0 $\pm$ 1.3	64.9 $\pm$ 1.9
Brick D	10	48.5 $\pm$ 1.2	58.0 $\pm$ 2.8	64.1 $\pm$ 2.5
	20	48.0 $\pm$ 1.3	54.6 $\pm$ 0.9	63.9 $\pm$ 2.9
	30	42.3 $\pm$ 0.6	51.8 $\pm$ 1.6	59.2 $\pm$ 1.9
Brick L	10	47.5 $\pm$ 3.4	56.9 $\pm$ 2.0	60.4 $\pm$ 1.8
	20	43.4 $\pm$ 3.5	51.8 $\pm$ 4.5	55.6 $\pm$ 2.9
	30	38.7 $\pm$ 1.6	50.0 $\pm$ 3.7	49.5 $\pm$ 2.0
Brick P	10	51.3 $\pm$ 1.7	64.7 $\pm$ 3.5	67.8 $\pm$ 3.0
	20	47.5 $\pm$ 1.1	57.8 $\pm$ 3.5	64.1 $\pm$ 1.2
	30	37.7 $\pm$ 2.9	56.1 $\pm$ 3.1	60.8 $\pm$ 1.2

CHAPTER THREE

MATERIALS

The materials used for this study were all obtained in Ghana. The limestone deposit is located at Oterkpolu in the Eastern region, the clam shells at DoforGbokpor in the Volta region, clay from Mankranso in the Ashanti region, and steel slag was obtained from Wahome Steel works in Tema in the Greater-Accra region. The other materials included CEM I Portland cement (Class 42.5N), crushed granitic aggregates, and river pit sand used locally for constructional works. The physical properties and chemical composition of the materials were determined during the study.

3.1 Oterkpolu limestone

The limestone deposit is located about 6.5 kilometers east of Oterkpolu village, which is about 25km from Koforidua, in the Eastern region of Ghana. It occurs within the arenaceous rocks of the Lower Voltaian range. The limestone is overlain by brown sandstone containing small iron-rich concretions which weather out to give a characteristically pitted surface with a purplish coloured transition zone at the base of the limestone. The rocks dip eastward into the hillside at angles from 20° and beyond, however, local variations may occur due to folding. Several investigations by the Ghana Geological Survey have estimated reserves of limestone at Oterkpolu to be over 3.7 million tonnes (Kesse, 1985). The limestone is grey in colour with a specific gravity of 2.76 as indicated in Table 3.1. The chemical composition of the limestone, determined during the study, contains about 42% CaO (indicating a CaCO₃ content of about 74.7%), 17% SiO₂ and 6.5% Fe₂O₃, as shown in Table 3.2. X-ray diffraction pattern of Oterkpolu limestone (Fig. 3.1) shows that the limestone consists

mainly of calcite (CaCO_3), the essential mineral needed for hydration effect on cement (Hawkins, 2003), and quartz.

Table 3.1: Physical Properties of Materials

Property	Reference cement	Limestone	Clam shells	Steel slag	Mankranso Clay	Pozzolana
Colour	Grey	grey	white	deep grey	Yellow	Red
Specific Gravity	3.16	2.76	2.82	2.85	2.64	2.59
Particle size of milled admixtures, %						
<0.002 mm		-	-	-	32	35
0.002 – 0.06 mm		76	85	30	30	62
0.05 mm – 0.6 mm		20	14	70	38	3

Table 3.2: Chemical composition of Materials

Chemical compound	Reference cement	Limestone	Steel slag	Clam shells	Clay	Pozzolana
SiO_2	18.80	17.27	21.31	2.10	59.95	62.08
Al_2O_3	3.57	0.03	7.50	0.25	0.82	7.23
Fe_2O_3	4.36	4.58	31.52	0.50	6.51	9.96
MgO	1.89	0.05	7.61	0.60	1.30	0.31
CaO	57.04	41.97	12.44	52.41	0.14	5.01
Na_2O	4.78	1.20	4.30	0.77	1.60	1.70
K_2O	4.43	2.58	1.03	1.68	1.29	1.92
MnO	0.14	0.07	5.29	0.06	0.12	0.02
TiO_2	0.16	1.05	0.05	0.16	1.05	0.10
P_2O_5	0.22	0.04	1.20	0.05	0.23	1.66
Cl	0.01	0.01	0.00	0.01	0.01	0.21
SO_3	0.85	0.24	0.26	0.35	0.07	0.30
LOI	3.60	31.00	7.50	41.07	26.00	9.50

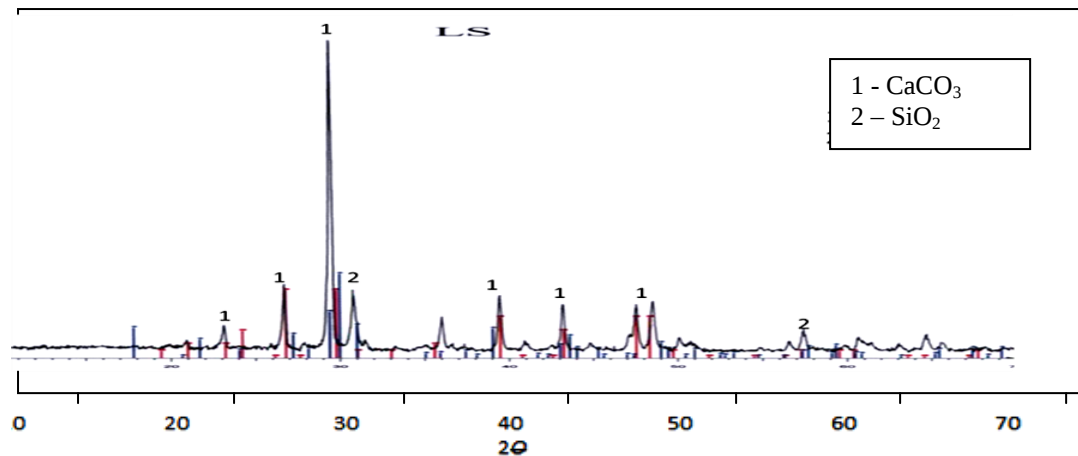


Figure. 3.1: X-Ray diffraction graph of Oterkpolu limestone

3.2 Clam shells

Clam shells are found in large deposits, usually interbedded with loose soil, along both the southern banks and the bed of the Volta river from Akuse to Ada in the Eastern, Greater-Accra and Volta regions of Ghana. They are mined and sold in the raw state to the poultry and mining industries. A small proportion of the mined shells are burnt and sold as lime for whitewashing of buildings. Clam shells are the purest source of calcium carbonate in Ghana. The shell deposit is estimated at more than 4 million tonnes (Kesse, 1985). The shell becomes very white in colour when washed. The main chemical compound is CaO (52.4%) and mineralogically contains calcite (Fig. 3.2).

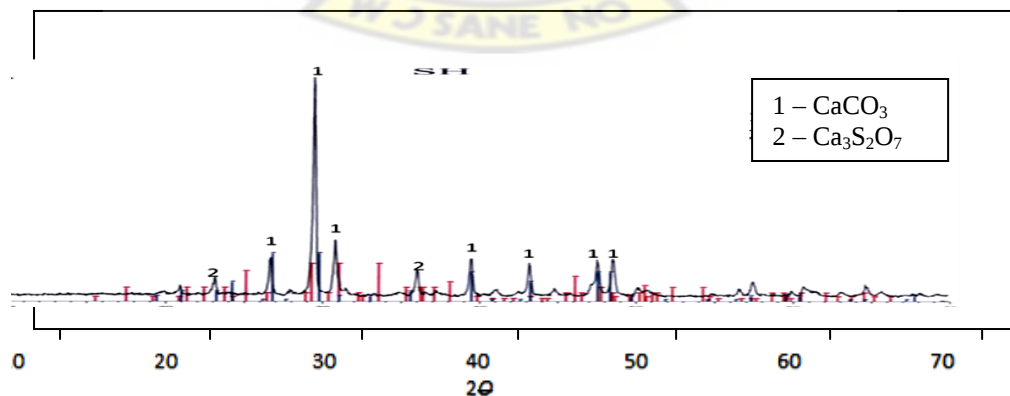


Figure. 3.2: X-Ray diffraction graph of clam shells

3.3 Steel slag

The steel slag samples were collected from Wahome Steel Company Ltd in Tema. It is regarded as a waste product in the production of structural steel sections and reinforcing bars. There are four main steel companies in Ghana, namely Wahome Steel Ltd, Western Steel and Forgings Limited, Ferro Fabric Gh Ltd, and Tema Steel Works all in Tema, which produce more than 5,000 tonnes of slag waste annually. Some of these companies have been in operation for more than 20 years. Due to increasing activities in infrastructure development, the tonnage of steel produced in Ghana is increasing. The wastes are dumped haphazardly at refuse sites, creating environmental nuisance and hazards in the areas. Chemical analysis of the sample showed it contains 31.5% Fe_2O_3 , 21.3% SiO_2 and 12.4% CaO . The main minerals are wustite, portlandite, calcite, quartz and belite (Fig. 3.3).

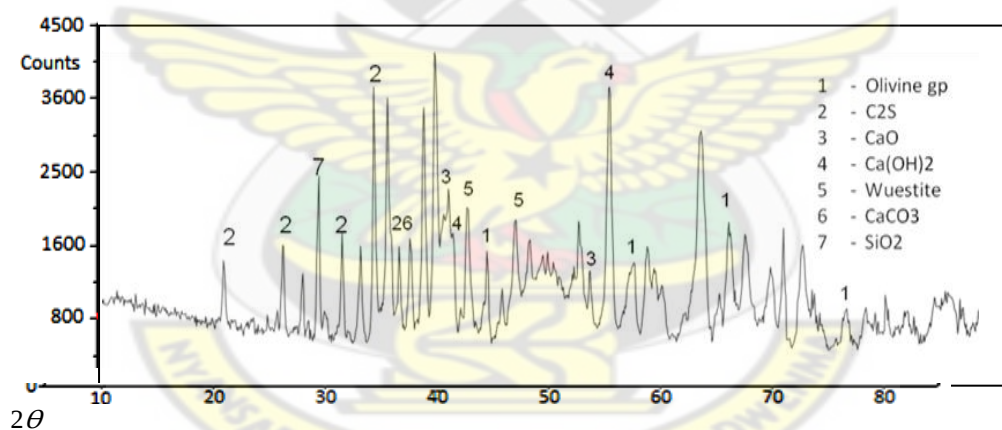


Figure 3.3: X-Ray Diffraction graph of Wahome steel slag

3.4 Mankranso clay

The clay sample was obtained from Mankranso which is located about 41km west of Kumasi on the Kumasi - Sunyani road. The clay is derived from the weathering of Lower Birimian (Middle Precambrian) phyllites, schists, tuff and greywacks and is yellow in colour (Kesse, 1985). The deposit area is drained by the Mankranriver and has an overburden thickness of less than 0.2m. The clay deposit spans more than 10 km

on both sides of the Kumasi - Sunyani road. The Mankranso clay is presently used by CSIR-Building and Road Research Institute for pozzolana production and by small-scale industries for the production of burnt bricks for housing construction.

The main minerals obtained from X-RD analysis are kaonilite, quartz, geothite and chlorite. The silica and iron oxide contents, from the chemical analysis (Table 3.2) of the clay were 59.9% and 6.5% respectively.

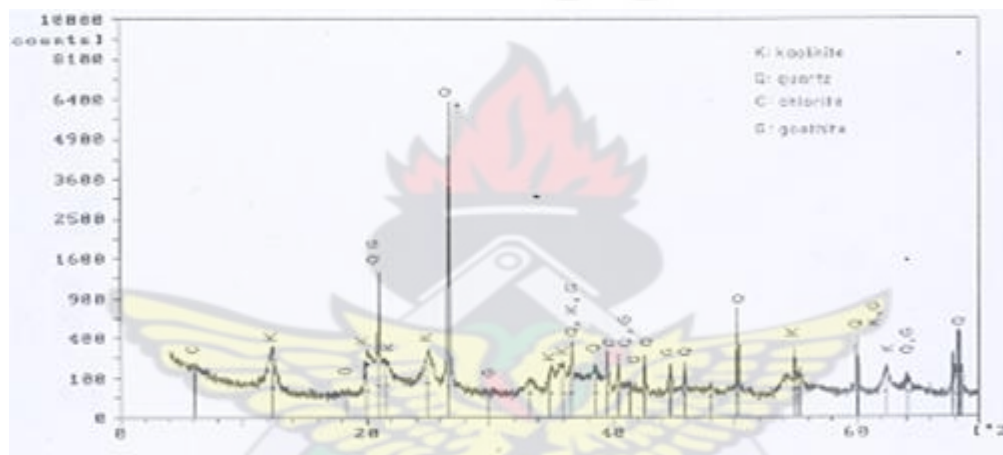


Figure. 3.4: X-Ray diffraction graph of Mankranso clay

3.5 Cement

The cement used for the study was CEM I Class 42.5N, produced by GHACEM Ltd, Ghana. It is used in Ghana for the construction of housing facilities, drains, culverts, bridges, flyovers, among others and satisfies all specifications of EN 197-1. The chemical (oxide) composition of the cement as given shows 57% CaO, and 18.8% SiO₂ content.(Table 3.2).The alumina (Al₂O₃) and iron oxide (Fe₂O₃) contents were 3.57% and 4.36% respectively. Table 3.3 gives the mineralogical composition and moduli of the reference cement with total calcium silicate content of 77.62 and a silica modulus (SR) of 1.39.

Table 3.3: Mineralogical composition and moduli of reference cement

Bogue potential composition, %				Moduli			
C_3S	C_2S	C_3A	C_4AF	LSF	AR	SR	HM
59.25	18.37	7.57	11.54	93.42	2.42	1.39	2.11

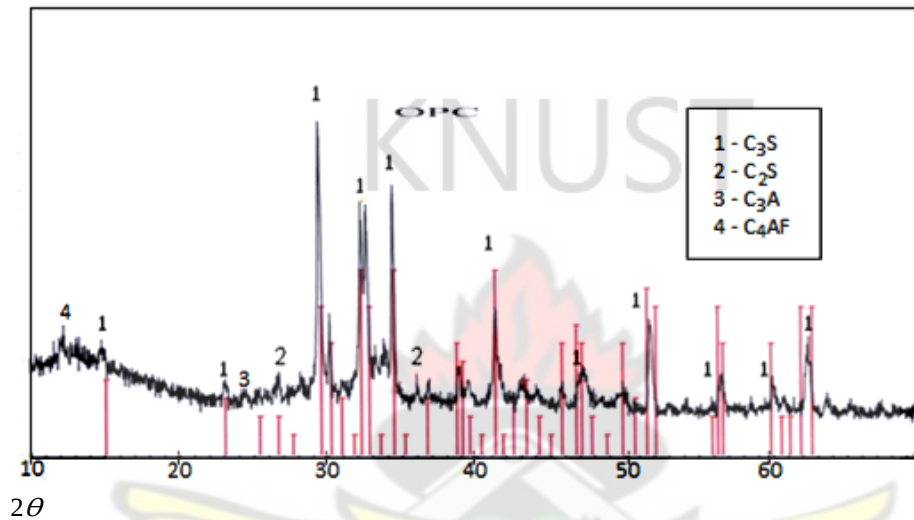


Figure. 3.5: X-Ray diffraction graph of ordinary Portland cement

CHAPTER FOUR

METHODS

4.0 Introduction

This section describes the various experimental methods adopted to determine and analyse the physical, chemical, mineralogical, mechanical and engineering properties of blended cements and very essential ones of the materials used for this study. It is important to obtain these properties in order to ascertain the suitability of the materials for the specific objectives of this study.

The test methods and analysis adopted conformed to those specified by International Standards Organisation (ISO), European Standards (CEN), British Standards (BS), Indian Standards (IS), Ghana Standards (GS) and other conventional standard methods.

4.1 Physical Properties

4.1.1 Moisture Content

The moisture contents of the clay sample were determined in accordance with BS 1377 (1990). About 30g of the natural clay from the site was placed in a covered container of known weight (m_1) and weighed (m_2). The container containing the clay was uncovered, and together with the cover was placed in an electric oven and dried at 105°C for 4 hours. The container with the clay was taken out, covered and placed in a dessicator to cool, after which it was weighed again (m_3). The moisture content, MC, of the sample was calculated as:

$$MC = \frac{m_2 - m_3}{m_3 - m_1} \times 100\% \quad 4.1$$

4.1.2 Particle Size Distribution

The particle size distribution for each of all four materials under investigations was determined by the hydrometer method of sedimentation as specified by BS 1377. About 500g of the samples were air-dried for 48 hours. After that about 200g of air-dried sample was passed through a 2.36mm standard sieve and the undersize dried in an oven at 105°C for 4 hours. The dry sample was then quartered and 50g of it was transferred into a 600-ml brass container. 100 ml of a dispersant solution, made from 7g of sodium metahexaphosphate and 33g of sodium oxalate in 1000 ml of distilled water, was added to the clay and made up to 250 ml with distilled water.

The suspension was agitated with a vibrating stirrer for 15 minutes and later transferred to a 1000-ml measuring cylinder. The contents were made up to 1000 ml with distilled water and left to stand for 24 hours to effect the decoagulation of the various soil particles. The cylinder was agitated manually for a minute to disperse the particles and placed on a bench. The timer was immediately switched on. The hydrometer was then immersed in the suspension and allowed to float upright. The hydrometer readings were first taken at 30 seconds and then at 1 minute, 2 minutes, 4 minutes and specific intervals for 8 hours and at 24 hours. Afterwards, the sample was washed through a 75µm sieve and the retained was dried at 105°C for 24 hours. The dry sample was passed through 2.4, 1.2, 0.6, 0.4, 0.2, 0.15 and 0.075mm standard sieves and the mass of fractions retained on each sieve were recorded.

4.1.3 Materials Preparation

In order to carry out the remaining tests of the study the raw materials were prepared and blended as described subsequently. The clam shells, steel slag and limestone were separately crushed and milled in a hammer mill for one hour and then passed through a 75 μ m BS standard sieve. The under-size were bagged, labelled and used for the study. The clam shells were thoroughly washed, to get rid of the dirt, before grinding. The clay samples were milled, nodulised and fired in a kiln at the optimum temperature of 800°C according to the works of Atiemo (2005) to produce a pozzolanic material. The calcined clay nodules were milled in a pulveriser and bagged for subsequent test preparation.

4.1.3.1 Mix Design of blended cement

The milled and sieved mineral admixtures (limestone, clam shells, clay pozzolana and steel slag) were blended with the Class 42.5N Portland cement using various mix designs given in Table 4.1. 5% of reference cement was first replaced by the four admixtures in turn to form the binary mix. Secondly, 10% cement was replaced by 5% by mass each of the two admixtures (ternary mix); for example, 5% by mass of cement was replaced by slag and 5% by mass of limestone constituting 10% cement replacement. Then, a cement replacement of 15% by either 5% each of the three admixtures was made constituting a quaternary mix or 10% replacement by one material and 5% by another admixture. A quinternary blend was obtained by replacing reference cement by 2.5% or 5% each of the admixtures. The blended cement samples, as presented in Table 4.1, were used to produce cement paste, mortar and concrete samples respectively for the study.

Table 4.1: Mix designs of blended cements for tests

Sample/	Material, %				
Type	Cement	Slag	Pozzolana	Shells	Limestone
Reference	100	-	-	-	-
	95	5	-	-	-
Binary	95	-	-	5	-
	95	-	-	-	5
	95	-	5	-	-
	90	5	-	5	-
	90	5	5	-	-
	90	-	5	5	-
	90	5	-	-	5
	90	-	5	-	5
	90	-	-	5	5
	85	10	-	5	-
Ternary	85	5	-	10	-
	85	-	10	5	-
	85	-	5	10	-
	85	10	5	-	-
	85	5	10	-	-
	85	-	10	-	5
	85	-	5	-	10
	85	-	-	5	10
	85	-	-	10	5
	85	10	-	-	5
	85	5	-	-	10
	80	10	-	10	-
	80	-	10	10	-
	80	10	10	-	-
	80	10	-	-	10
	80	-	10	-	10
	80	-	-	10	10
	92.5	2.5	2.5	2.5	-
	92.5	2.5	2.5	-	2.5
	92.5	2.5	-	2.5	2.5
	92.5	-	2.5	2.5	2.5
Quaternary	85	5	5	5	-
	85	5	5	-	5
	85	5	-	5	5
	85	-	5	5	5
Quinternary	90	2.5	2.5	2.5	2.5
	80	5	5	5	5

4.1.4 Specific Gravity

Determination of the specific gravity of materials in cement concrete is necessary in calculating the percentage of voids and the solid volume of aggregates in computations of yield. The determination of specific gravity of the raw and all cement samples were carried out as specified by BS 1377 (1990). A 50-ml density bottle with the stopper was dried at 105°C in an oven for 24 hrs and weighed (m_1). 25g of ground, oven-dried sample, which had been passed through 75µm sieve, was transferred into the density bottle. The bottle and its contents with the stopper were weighed again (m_2). The bottle was then half-filled with kerosene. The container was afterwards placed in a vacuum dessicator, with the stopper removed, and the air in the container gradually evacuated. When no air was seen to be released, the bottle was removed and weighed (m_3). The bottle was afterwards emptied of its contents, cleaned and completely filled with kerosene, stoppered and reweighed (m_4). The specific gravity (G_s) of the sample was calculated as:

$$G_s = \frac{G_L(m_2 - m_1)}{(m_4 - m_1) - (m_3 - m_1)} \times 100\% \quad 4.2$$

where G_L = specific gravity of kerosene.

4.1.5 Soundness Test

After cement has set it must not undergo any appreciable expansion beyond 10mm, which could disrupt a mortar or concrete. It is a measure of durability of cement. The soundness test was done in accordance with the EN 196-3 (2000) specified method. Cement paste of standard consistency was prepared. A lightly-oiled Le Chatelier mould was placed on a lightly-oiled glass plate and filled immediately with the blended cement paste to the top surface. The mould was covered with the lightly oiled glass plate, a standard small weight placed on it and then the complete

apparatus was immediately placed in the humidity cabinet. The cabinet environment was maintained at $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and not less than 98% relative humidity for $24\text{ h} \pm 0.5\text{ h}$.

At the end of the period, the distance (A) between the indicator points was measured to the nearest 0.5mm. The mould was gradually heated to boiling during $(30 \pm 5)\text{ min}$ and the water-bath was maintained at boiling temperature for $3\text{ h} \pm 5\text{ min}$. At the end of the boiling period the distance (B) between the indicator points was measured to the nearest 0.5mm. The method was repeated. The difference between B and A was recorded and the mean of the 2 values of the difference calculated.

The percentage expansion (E) was calculated as:

$$E = \frac{B - A}{A} \times 100\% \quad 4.3$$

4.1.6 Water permeability

Water permeability is a measure of the porosity of cement products and gives indication of ease of attack of such products by aggressive fluids. In the present study, the overall porosity is determined by water absorption which measures the pore space indirectly by the procedure given in ASTM C 642-90 by oven-drying. For this test, $100\text{ mm} \times 100\text{ mm} \times 100\text{ mm}$ size concrete cubes were cast in duplicate. After demoulding, the specimens were kept immersed in water. The experiment was conducted at the end of 28 days evaluate the effect of curing on overall porosity. At the end of curing period, the specimens were taken from the curing tank and air-dried to remove surface moisture. After this, the specimens were dried in an oven at a temperature of $100 \pm 10^{\circ}\text{C}$ for 48h, allowed to cool to room temperature, and the weight of the

specimens measured to an accuracy of 1g using a digital balance. Then the specimens were kept immersed in water for one hour and the increase in weight was measured. From this the co-efficient of water absorption was calculated using the following formula.

$$K_a = \frac{Q / A^{\frac{1}{2}}}{t} \quad 4.4$$

Where K_a is the co-efficient of water absorption, Q the quantity of water absorbed by the oven-dry specimen in time, t , and A the total surface area of concrete specimen through which water penetrates, $t=60$ min. The co-efficient of water absorption was calculated for each curing period.

4.1.7 Water Demand

The Vicat method, specified by EN 197-3 (2000), was used to determine the water demand and setting times of the various reference and blended cement pastes. This method gives the quantity of water needed to produce a cement paste of standard consistency and also for the setting times of the cements.

The Vicatmould, resting on a non-porous plate, was filled completely with the blended cement paste in one layer and the surface smoothened off level with the top of the mould as quickly as possible. The test block, confined in the mould and resting on the plate was placed under the rod bearing the plunger. The plunger was lowered gently into contact with the surface of the test block and quickly released and allowed to sink in. Trial blended cement pastes, made with varying amounts of water, were used until the plunger settled at 6mm from the bottom of the mould. The

amount of water used was recorded as standard consistency (water demand) and expressed as a percentage by mass of the dry cement.

4.1.8 Setting Time

The setting of cement is used to describe the stiffening of cement paste which is mainly caused by the hydration of C_3A compounds in cement. The initial setting time is the interval between the mixing of the cement with H_2O and the time when the mix loses its plasticity, stiffening to a certain degree. It marks the end of the period when the wet mix can be moulded into shape. The final setting time is the point at which the set cement has acquired a sufficient firmness to resist a certain defined pressure. The amount of water, in percentage, to reach the normal stiffness is the water demand of the cement.

4.1.8.1 Initial Setting Time

The Vicat method was used for the determination of the initial setting time of the blended cement. Here, the cement paste, using the percentage of water recorded for the standard consistence, was gauged into the Vicatmould. The test block, confined in the mould and resting on the plate, was placed under the rod bearing the needle. The needle was then lowered gently into contact with the surface of the test block and quickly released and allowed to sink in. This process was repeated until the needle, when brought into contact with the test block and released as described above, did not penetrate beyond a point approximately 5mm from the bottom of the mould. The period elapsed between the time when the water was added to the cement and the time at which the needle ceased to pierce the test block beyond the prescribed depth was noted as the initial setting time.

4.1.8.2 Final Setting Time

For the determination of the final setting time, the needle used for the initial setting time was replaced by the needle with an annular attachment in the Vicat apparatus. The cement was considered as finally set when, upon applying the needle gently to the surface of the test block, only the needle made an impression, while the attachment failed to do so. The time lapse at which the needle ceased to pierce the test block, as described above, was noted as the final setting time.

4.2 Chemical Properties

The chemical compositions of the mineral admixtures and cement were determined by X-ray Fluorescence analysis using Spectro X-LAB 2000 equipment at the Ghana Geological Survey Department in Accra. The admixtures and ordinary Portland cement were blended separately at specific proportions and packaged. 4g of the blended sample presented was measured and placed in a special vessel purposely made for this kind of analysis. About 0.9g of Hoechst Micro powder was then added to blend, and the resulting mixture put in a mill. Two small round balls were added to the resulting mixture before placing it in the mill. The purpose of the milling phase was to reduce particles size further to about 100 microns and preferably less. The action of the mill also helped to achieve a homogeneous mixture.

The balls which assisted to reduce the particle size were then removed, and the remaining mixture placed in a die. The die was placed in a press, and a force of between 5 to 8 tonnes applied to produce the pellet for the chemical analysis.

4.3 Mineralogical Properties

The various minerals present in the test materials and the hydrated products of reference and blended cements were determined and analysed using infrared spectrometry (IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray (EDX) and thermoanalysis methods (TG/DTA).

4.3.1 Infrared Spectrometry Analysis

Infrared spectroscopy is used to identify compounds or investigate sample composition. It exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy level (vibrational modes). The infrared spectrum of a sample is collected by passing a beam of infrared light through the sample. From this, an absorbance can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. This technique works almost exclusively on samples with covalent bonds (Demirdöven *et al*, 2004).

IR analysis was used for the study to determine the effect of admixtures during cement hydration. The infrared analysis was recorded with hydrated blended cements at 7 and 28 days respectively. 2mg of the solid sample (blended cement) that was obtained was mixed with 400mg of potassium bromide powder in an agate mortar. 200mg of the mixture was then pressed for about 5 minutes into a pellet (disc) using a special mould and a hydraulic press with an estimated force of about 8 tonnes. The pellet was then passed through a FTIR-8201A single beam laser Shimadzu Infrared Spectrophotometer, where the specific functional groups were determined. The

samples were analysed at the Physical Science Department of the University of Cape Coast.

4.3.2 X-Ray Diffraction Analysis

X-ray Diffraction (XRD) analysis is a non-destructive analytical method by which X-rays of a known wavelength are passed through a sample in order to identify the crystal structure, chemical composition, and physical properties of the sample. The wave nature of the X-rays means that they are diffracted by the lattice of the crystal to give a unique pattern of peaks of 'reflections' at differing angles and of different intensity, just as light can be diffracted by a grating of suitably spaced lines.

For this study, the hydrated cement blend was removed from water at the test date and immersed in acetone to stop hydration. About 0.5g of the cement specimen was then ground to a mesh size of below 75 μ m and pressed into the holder with a 10mm x 30mm thin glass plate using the thumb. The holder was then placed in a PHILIPS PW 1830 X-ray diffractometer for the determination. The tests were performed at the Materials Science Dept. Laboratory of the University of Manchester, in the United Kingdom.

4.3.3 Scanning Electron Microscopic (SEM) analysis

Scanning electron microscopy (SEM) is a technology used in studying the microstructure of cement paste. The electron microscope images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that

contain information about the sample's surface topography, composition and other properties such as electrical conductivity (Stultzman, 2004).

The cement specimens were removed from water and acetone was added to them to inhibit hydration. The specimens were broken and ground to powder (about 50µm). A few of the powder was spread thinly on the adhesive surface of the holder and placed in the ZEISS SEM analyser equipment for analysis.

4.3.4 Energy Dispersive X-ray Analysis (EDX)

Energy Dispersive X-ray (EDX) analysis is a modern technique used for identifying the elemental composition of the specimen, or an area of interest thereof. The EDX analysis system works as an integrated feature of a scanning electron microscope (SEM), and cannot operate on its own without the latter. During EDX Analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms' own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray.

The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity

of the atom from which the X-ray was emitted can be established. The output of an EDX analysis is an EDX spectrum. EDX spectrum plots how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen. An EDX spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well.

The samples were treated with acetone to halt hydration after 28 days and ground in an unglazed porcelain mortar and pestle to a particle size of less than $75\mu\text{m}$. The powders were applied smoothly and thinly on 5mm diameter magnetic holders, labelled and stored in sealed containers to prevent moisture exchange and carbonation. The SEM/EDX tests were performed at the Materials Science Laboratory of the University of Manchester, using a ZEIS SEM/EDX equipment (Fig. 4.1). The EDX analysis of the samples was performed simultaneously as the SEM analysis.



Figure 4.1 Scanning Electron Microscope/Energy Dispersive X-ray equipment

4.4 Thermoanalysis of cement

Thermoanalysis tests are performed to analyse behaviour of materials under heat treatment. Thermogravimetric analysis (TG) is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. In this study, the analysis was done to determine specifically the quantity of calcium hydroxide in the various cement samples.

Differential thermal analysis (DTA) is a thermoanalytic method where the material under study and an inert reference are heated (or cooled) under identical conditions, while recording any temperature difference between sample and reference. This differential temperature is then plotted against time, or against temperature (DTA curve or thermogram). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation (Lea, 1970; Taylor, 1997).

Simultaneous TGA-DTA analysis measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization) and those which involve a weight loss (e.g., degradation). The sample preparation and TGA/DTA tests and analysis were performed using a Seiko SSC5200 and

MettlerToledo TGA/DSC1 equipment at the Physical and Micro Analytical Laboratories, School of Chemistry, of the University of Manchester, UK.

The samples were ground in an unglazed porcelain mortar and pestle. The powders were stored in small screw-cap glass vials and labelled. The size range of the powder was such that 70-80% of it was between 149 μ m to 74 μ m. The remaining 30-20% was finer. The tests were done one after the other. Approximately 9.7 mg of a ground sample was placed in the quartz bucket and weighed accurately to the nearest 0.1 mg. Dry nitrogen at a flow rate of 100ml/min passed over the sample and heat applied from 25°C to 1000°C at 20°C/min for 10 minutes. The electromotive force (e.m.f.) equivalent to the weight change, and the e.m.f. equivalent to the temperature which was measured was displayed and the TGA/DTA/DTG graphs plotted simultaneously. During calcinations the sample lost weight because of the thermal decomposition of inherent compounds. After calcination, the sample of oxide was cooled to room temperature and evacuated

4.5 Mechanical Properties

4.5.1 Compressive, tensile strength and water absorption

The compressive strength of mortar is mostly used as a principal criterion for selecting mortar type, since compressive strength is relatively easy to measure, and it commonly relates to some other properties, such as tensile strength of the mortar. The tensile strength is a measure of an unreinforced concrete beam or slab to resist failure in tension. This strength is expressed as *modulus of rupture* and is usually between 10 and 20% of compressive strength (Dayaratnam, 1999). Other property

determined was the water absorption when the mortar samples were immersed in seawater and 5% Na₂SO₄ solution.

4.5.1.1 Batching, mixing and casting

Sufficient quantities of Class 42.5N Portland cement, clay pozzolana, limestone, clam shells, steel slag, aggregates and water for batches to produce five (5) cubes and prism specimens were measured by mass as per the mix proportions. The fine and coarse aggregates were sampled from large lots by quartering before batching.

Blended cement (given in Table 4.1) to sand ratio of 1:3, and water to cement ratio of 0.5 were used to prepare all mortar samples. The materials for each mortar sample were mixed separately. The blended cement was mixed with the measured quantity of sand. Afterwards, the quantity of water needed was added and mixed for about 4 minutes. The mortar was tamped in the moulds and then vibrated for 2 minutes. After gauging, the mould was covered with a metal plate and a damp hessian sack. For the concrete test, 1:2:4 cement, fine and coarse aggregate ratio, and water to cement ratio of 0.6 were used to produce the concrete samples. In all, the test samples included 75mm cement mortar cubes, 100mm concrete cubes and 150mm x 310mm concrete cylindrical specimens were prepared for the compressive tests. 50mm x 50mm x 150mm concrete prisms were prepared for flexural tensile tests using BS and EN specifications. All the experiments were done at a room temperature of approximately $27^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and $70\% \pm 2\%$ relative humidity. The mortar cubes, concrete cubes and prisms were removed from their moulds 24 hours after gauging and weighed. The weighed cubes were then immersed in a pond of water of average temperature of $22^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and kept for the specified testing periods.

In all, 1075 mortar and 620 samples were prepared for the compressive tests, and 510 mortar samples for the durability. Five samples were tested for each age date.

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4.5.1.2 Slump Test

This test was used to determine the workability of the fresh concrete. The steel mould for the slump test was a frustum of a cone, 300mm high. The mould was thoroughly cleaned and placed on a smooth levelled surface with an opening of diameter 100mm at the top and 200mm at the bottom. It was firmly held against its base and filled with concrete in three layers. Each layer was tamped 25 times with a standard 16mm diameter steel rod that was rounded at the end. The excess concrete was struck off the top and the base was cleared of all droppings. The cone was steadily lifted vertically. A straight edge was placed on top of the inverted empty cone placed alongside the slumped concrete. The slump was measured as the difference between the highest point of the slumped concrete and the underside of the straight edge.

4.5.1.3 Strength tests

The cement mortar and concrete cube and cylindrical specimens were tested for their compressive strengths at 2, 7, 28, 90 and 365 days using a universal testing machine in accordance with EN 197-2 (2000). The flexural tensile strengths of the concretes from the cement blends were determined from the prisms prepared. The modulus of rupture was calculated based on the of elastic theory using the formula:

$$F_{pc} = \frac{PL}{bd^2} \quad 4.5$$

Where F_{pc} = modulus of rupture in N/mm^2 ; P = load (force); L = effective span; b = width of the beam; and d = thickness

4.5.1.4 Water Absorption

The water absorption of the cement mortar cubes, concrete cubes and prisms was determined by weighing the cubes immediately after removing them from their moulds to give the initial mass, m_1 . The cubes were then immersed in water for 28 days. The mass of the wet cubes, m_2 , were then taken before their compressive strengths were tested. The water absorption, w , of the cubes was calculated as;

$$w = \frac{m_2 - m_1}{m_1} \times 100\% \quad 4.7$$

4.6 Durability Tests

Durability of cements and their products refers to their ability to withstand extreme or excessive deleterious conditions which otherwise will affect their required structural performance and resilience. The long-term durability of cementitious materials is mostly dependent upon their physical and chemical properties. It is recognized that the more important prerequisite is reducing the permeability of material to the ionic species. C_3A -related compounds are given much attention when it comes to cement durability because sulfate resistance and the chloride binding capacity of cement products depend on the stability of C_3A hydrates formed before the attack (Bonavettiet *al*, 2001). In sulfate attack, ettringite formed prior to the immersion in sulfate solution will be a stable phase while the monosulfoaluminate and the monocarboaluminate will be unstable phases.

4.6.1 Sulphate and Chloride Resisting Tests

Cement products, especially concretes and mortars, are attacked by acidic media, and are severely affected by sulphates and chlorides which are found in the soil and/or groundwater. These acids affect the cement structures negatively through chemical actions leading to expansion and corrosion of reinforced steel that eventually result in loss of strength and durability. It is therefore essential to determine the performance of cements in these acidic media so as to determine their durability (O'Farrel, *et al*, 1999, Osborne, 1999).

Cement mortar cubes produced as in 4.51.1 – 4.51.3 were immersed in 5% Na₂SO₄ solutions and sea water for 28, 90 and 365 days. The cubes were examined visually, photographed and their compressive strengths determined.

4.6.2 Strength Deterioration Factor (SDF)

The deterioration of the mortar cubes was investigated by determining the strength deterioration factor due to the sulphate and chloride attack was determined using the formula by Murthi and Sivakumar (2008):

$$SDF = \frac{(f_{cw} - f_{ca})}{f_{cw}} \quad 4.7$$

where f_{cw} = the average compressive strength of cubes in water

f_{ca} = the average compressive strength of cubes in acidic solution

The cubes were tested for compressive strength at 28, 180 and 365 days according to EN 196-2 (2000).

CHAPTER FOUR

METHODS

4.0 Introduction

This section describes the various experimental methods adopted to determine and analyse the physical, chemical, mineralogical, mechanical and engineering properties of blended cements and very essential ones of the materials used for this study. It is important to obtain these properties in order to ascertain the suitability of the materials for the specific objectives of this study.

The test methods and analysis adopted conformed to those specified by International Standards Organisation (ISO), European Standards (CEN), British Standards (BS), Indian Standards (IS), Ghana Standards (GS) and other conventional standard methods.

4.1 Physical Properties

4.1.1 Moisture Content

The moisture contents of the clay sample were determined in accordance with BS 1377 (1990). About 30g of the natural clay from the site was placed in a covered container of known weight (m_1) and weighed (m_2). The container containing the clay was uncovered, and together with the cover was placed in an electric oven and dried at 105°C for 4 hours. The container with the clay was taken out, covered and placed in a dessicator to cool, after which it was weighed again (m_3). The moisture content, MC, of the sample was calculated as:

$$MC = \frac{m_2 - m_3}{m_3 - m_1} \times 100\% \quad 4.1$$

4.1.2 Particle Size Distribution

The particle size distribution for each of all four materials under investigations was determined by the hydrometer method of sedimentation as specified by BS 1377. About 500g of the samples were air-dried for 48 hours. After that about 200g of air-dried sample was passed through a 2.36mm standard sieve and the undersize dried in an oven at 105°C for 4 hours. The dry sample was then quartered and 50g of it was transferred into a 600-ml brass container. 100 ml of a dispersant solution, made from 7g of sodium metahexaphosphate and 33g of sodium oxalate in 1000 ml of distilled water, was added to the clay and made up to 250 ml with distilled water.

The suspension was agitated with a vibrating stirrer for 15 minutes and later transferred to a 1000-ml measuring cylinder. The contents were made up to 1000 ml with distilled water and left to stand for 24 hours to effect the decoagulation of the various soil particles. The cylinder was agitated manually for a minute to disperse the particles and placed on a bench. The timer was immediately switched on. The hydrometer was then immersed in the suspension and allowed to float upright. The hydrometer readings were first taken at 30 seconds and then at 1 minute, 2 minutes, 4 minutes and specific intervals for 8 hours and at 24 hours. Afterwards, the sample was washed through a 75µm sieve and the retained was dried at 105°C for 24 hours. The dry sample was passed through 2.4, 1.2, 0.6, 0.4, 0.2, 0.15 and 0.075mm standard sieves and the mass of fractions retained on each sieve were recorded.

4.1.3 Materials Preparation

In order to carry out the remaining tests of the study the raw materials were prepared and blended as described subsequently. The clam shells, steel slag and limestone were separately crushed and milled in a hammer mill for one hour and then passed through a 75µm BS standard sieve. The under-size were bagged, labelled and used for the study. The clam shells were thoroughly washed, to get rid of the dirt, before grinding. The clay samples were milled, nodulised and fired in a kiln at the optimum temperature of 800°C according to the works of Atiemo (2005) to produce a pozzolanic material. The calcined clay nodules were milled in a pulveriser and bagged for subsequent test preparation.

4.1.3.1 Mix Design of blended cement

The milled and sieved mineral admixtures (limestone, clam shells, clay pozzolana and steel slag) were blended with the Class 42.5N Portland cement using various mix designs given in Table 4.1. 5% of reference cement was first replaced by the four admixtures in turn to form the binary mix. Secondly, 10% cement was replaced by 5% by mass each of the two admixtures (ternary mix); for example, 5% by mass of cement was replaced by slag and 5% by mass of limestone constituting 10% cement replacement. Then, a cement replacement of 15% by either 5% each of the three admixtures was made constituting a quaternary mix or 10% replacement by one material and 5% by another admixture. A quinternary blend was obtained by replacing reference cement by 2.5% or 5% each of the admixtures. The blended cement samples, as presented in Table 4.1, were used to produce cement paste, mortar and concrete samples respectively for the study.

Table 4.1: Mix designs of blended cements for tests

Sample/	Material, %
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Type	Cement	Slag	Pozzolana	Shells	Limestone
Reference	100	-	-	-	-
	95	5	-	-	-
Binary	95	-	-	5	-
	95	-	-	-	5
	95	-	5	-	-
	90	5	-	5	-
	90	5	5	-	-
	90	-	5	5	-
	90	5	-	-	5
	90	-	5	-	5
-	90	-	-	5	5
	90	-	-	5	5
Ternary	85	10	-	5	-
	85	5	-	10	-
	85	-	10	5	-
	85	-	5	10	-
	85	10	5	-	-
	85	5	10	-	-
	85	-	10	-	5
	85	-	5	-	10
	85	-	-	5	10
	85	-	-	10	5
	85	10	-	-	5
	85	5	-	-	10
	80	10	-	10	-
	80	-	10	10	-
	80	10	10	-	-
	80	10	-	-	10
	80	-	10	-	10
	80	-	-	10	10
	92.5	2.5	2.5	2.5	-
	92.5	2.5	2.5	-	2.5
	92.5	2.5	-	2.5	2.5
	92.5	-	2.5	2.5	2.5
Quaternary	85	5	5	5	-
	85	5	5	-	5
	85	5	-	5	5
	85	-	5	5	5
Quinternary	90	2.5	2.5	2.5	2.5
	80	5	5	5	5

4.1.4 Specific Gravity

Determination of the specific gravity of materials in cement concrete is necessary in calculating the percentage of voids and the solid volume of aggregates in

computations of yield. The determination of specific gravity of the raw and all cement samples were carried out as specified by BS 1377 (1990). A 50-ml density bottle with the stopper was dried at 105°C in an oven for 24 hrs and weighed (m_1). 25g of ground, oven-dried sample, which had been passed through 75 μ m sieve, was transferred into the density bottle. The bottle and its contents with the stopper were weighed again (m_2). The bottle was then half-filled with kerosene. The container was afterwards placed in a vacuum dessicator, with the stopper removed, and the air in the container gradually evacuated. When no air was seen to be released, the bottle was removed and weighed (m_3). The bottle was afterwards emptied of its contents, cleaned and completely filled with kerosene, stoppered and reweighed (m_4). The specific gravity (G_s) of the sample was calculated as:

$$G_s = \frac{G_L(m_2 - m_1)}{(m_4 - m_1) - (m_3 - m_1)} \times 100\% \quad 4.2$$

where G_L = specific gravity of kerosene.

4.1.5 Soundness Test

After cement has set it must not undergo any appreciable expansion beyond 10mm, which could disrupt a mortar or concrete. It is a measure of durability of cement. The soundness test was done in accordance with the EN 196-3 (2000) specified method. Cement paste of standard consistency was prepared. A lightly-oiled Le Chatelier mould was placed on a lightly-oiled glass plate and filled immediately with the blended cement paste to the top surface. The mould was covered with the lightly oiled glass plate, a standard small weight placed on it and then the complete apparatus was immediately placed in the humidity cabinet. The cabinet environment

was maintained at $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and not less than 98% relative humidity for $24\text{ h} \pm 0.5\text{ h}$.

At the end of the period, the distance (A) between the indicator points was measured to the nearest 0.5mm. The mould was gradually heated to boiling during $(30 \pm 5)\text{ min}$ and the water-bath was maintained at boiling temperature for $3\text{ h} \pm 5\text{ min}$. At the end of the boiling period the distance (B) between the indicator points was measured to the nearest 0.5mm. The method was repeated. The difference between B and A was recorded and the mean of the 2 values of the difference calculated.

The percentage expansion (E) was calculated as:

$$E = \frac{B - A}{A} \times 100\% \quad 4.3$$

4.1.6 Water permeability

Water permeability is a measure of the porosity of cement products and gives indication of ease of attack of such products by aggressive fluids. In the present study, the overall porosity is determined by water absorption which measures the pore space indirectly by the procedure given in ASTM C 642-90 by oven-drying. For this test, $100\text{ mm} \times 100\text{ mm} \times 100\text{ mm}$ size concrete cubes were cast in duplicate. After demoulding, the specimens were kept immersed in water. The experiment was conducted at the end of 28 days evaluate the effect of curing on overall porosity. At the end of curing period, the specimens were taken from the curing tank and air-dried to remove surface moisture. After this, the specimens were dried in an oven at a temperature of $100 \pm 10^{\circ}\text{C}$ for 48h, allowed to cool to room temperature, and the weight of the specimens measured to an accuracy of 1g using a digital balance. Then the

specimens were kept immersed in water for one hour and the increase in weight was measured. From this the co-efficient of water absorption was calculated using the following formula.

$$K_a = \frac{Q / A^{\frac{1}{2}}}{t} \quad 4.4$$

Where K_a is the co-efficient of water absorption, Q the quantity of water absorbed by the oven-dry specimen in time, t , and A the total surface area of concrete specimen through which water penetrates, $t=60$ min. The co-efficient of water absorption was calculated for each curing period.

4.1.7 Water Demand

The Vicat method, specified by EN 197-3 (2000), was used to determine the water demand and setting times of the various reference and blended cement pastes. This method gives the quantity of water needed to produce a cement paste of standard consistency and also for the setting times of the cements.

The Vicatmould, resting on a non-porous plate, was filled completely with the blended cement paste in one layer and the surface smoothened off level with the top of the mould as quickly as possible. The test block, confined in the mould and resting on the plate was placed under the rod bearing the plunger. The plunger was lowered gently into contact with the surface of the test block and quickly released and allowed to sink in. Trial blended cement pastes, made with varying amounts of water, were used until the plunger settled at 6mm from the bottom of the mould. The amount of water used was recorded as standard consistency (water demand) and expressed as a percentage by mass of the dry cement.

4.1.8 Setting Time

The setting of cement is used to describe the stiffening of cement paste which is mainly caused by the hydration of C_3A compounds in cement. The initial setting time is the interval between the mixing of the cement with H_2O and the time when the mix loses its plasticity, stiffening to a certain degree. It marks the end of the period when the wet mix can be moulded into shape. The final setting time is the point at which the set cement has acquired a sufficient firmness to resist a certain defined pressure. The amount of water, in percentage, to reach the normal stiffness is the water demand of the cement.

4.1.8.1 Initial Setting Time

The Vicat method was used for the determination of the initial setting time of the blended cement. Here, the cement paste, using the percentage of water recorded for the standard consistence, was gauged into the Vicatmould. The test block, confined in the mould and resting on the plate, was placed under the rod bearing the needle. The needle was then lowered gently into contact with the surface of the test block and quickly released and allowed to sink in. This process was repeated until the needle, when brought into contact with the test block and released as described above, did not penetrate beyond a point approximately 5mm from the bottom of the mould. The period elapsed between the time when the water was added to the cement and the time at which the needle ceased to pierce the test block beyond the prescribed depth was noted as the initial setting time.

4.1.8.2 Final Setting Time

For the determination of the final setting time, the needle used for the initial setting time was replaced by the needle with an annular attachment in the Vicat apparatus. The cement was considered as finally set when, upon applying the needle gently to the surface of the test block, only the needle made an impression, while the attachment failed to do so. The time lapse at which the needle ceased to pierce the test block, as described above, was noted as the final setting time.

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For this study, the hydrated cement blend was removed from water at the test date and immersed in acetone to stop hydration. About 0.5g of the cement specimen was then ground to a mesh size of below 75 μ m and pressed into the holder with a 10mm x 30mm thin glass plate using the thumb. The holder was then placed in a PHILIPS PW 1830 X-ray diffractometer for the determination. The tests were performed at the Materials Science Dept. Laboratory of the University of Manchester, in the United Kingdom.

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The cement specimens were removed from water and acetone was added to them to inhibit hydration. The specimens were broken and ground to powder (about 50µm). A few of the powder was spread thinly on the adhesive surface of the holder and placed in the ZEISS SEM analyser equipment for analysis.

4.3.4 Energy Dispersive X-ray Analysis (EDX)

Energy Dispersive X-ray (EDX) analysis is a modern technique used for identifying the elemental composition of the specimen, or an area of interest thereof. The EDX analysis system works as an integrated feature of a scanning electron microscope (SEM), and cannot operate on its own without the latter. During EDX Analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms' own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray.

The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established. The output of an EDX analysis is an EDX spectrum. EDX spectrum plots how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks

corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen. An EDX spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well.

The samples were treated with acetone to halt hydration after 28 days and ground in an unglazed porcelain mortar and pestle to a particle size of less than $75\mu\text{m}$. The powders were applied smoothly and thinly on 5mm diameter magnetic holders, labelled and stored in sealed containers to prevent moisture exchange and carbonation. The SEM/EDX tests were performed at the Materials Science Laboratory of the University of Manchester, using a ZEIS SEM/EDX equipment (Fig. 4.1). The EDX analysis of the samples was performed simultaneously as the SEM analysis.



Figure 4.1 Scanning Electron Microscope/Energy Dispersive X-ray equipment

4.4 Thermoanalysis of cement

Thermoanalysis tests are performed to analyse behaviour of materials under heat treatment. Thermogravimetric analysis (TG) is performed on samples to determine

changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. In this study, the analysis was done to determine specifically the quantity of calcium hydroxide in the various cement samples.

Differential thermal analysis (DTA) is a thermoanalytic method where the material under study and an inert reference are heated (or cooled) under identical conditions, while recording any temperature difference between sample and reference. This differential temperature is then plotted against time, or against temperature (DTA curve or thermogram). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation (Lea, 1970; Taylor, 1997).

Simultaneous TGA-DTA analysis measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization) and those which involve a weight loss (e.g., degradation). The sample preparation and TGA/DTA tests and analysis were performed using a Seiko SSC5200 and MettlerToledo TGA/DSC1 equipment at the Physical and Micro Analytical Laboratories, School of Chemistry, of the University of Manchester, UK.

The samples were ground in an unglazed porcelain mortar and pestle. The powders were stored in small screw-cap glass vials and labelled. The size range of the powder was such that 70-80% of it was between 149 μ m to 74 μ m. The remaining 30-20% was finer. The tests were done one after the other. Approximately 9.7 mg of a ground sample was placed in the quartz bucket and weighed accurately to the nearest 0.1 mg. Dry nitrogen at a flow rate of 100ml/min passed over the sample and heat applied from 25°C to 1000°C at 20°C/min for 10 minutes. The electromotive force (e.m.f.) equivalent to the weight change, and the e.m.f. equivalent to the temperature which was measured was displayed and the TGA/DTA/DTG graphs plotted simultaneously. During calcinations the sample lost weight because of the thermal decomposition of inherent compounds. After calcination, the sample of oxide was cooled to room temperature and evacuated

4.5 Mechanical Properties

4.5.1 Compressive, tensile strength and water absorption

The compressive strength of mortar is mostly used as a principal criterion for selecting mortar type, since compressive strength is relatively easy to measure, and it commonly relates to some other properties, such as tensile strength of the mortar. The tensile strength is a measure of an unreinforced concrete beam or slab to resist failure in tension. This strength is expressed as *modulus of rupture* and is usually between 10 and 20% of compressive strength (Dayaratnam, 1999). Other property determined was the water absorption when the mortar samples were immersed in seawater and 5% Na₂SO₄ solution.

4.5.1.1 Batching, mixing and casting

Sufficient quantities of Class 42.5N Portland cement, clay pozzolana, limestone, clam shells, steel slag, aggregates and water for batches to produce five (5) cubes and prism specimens were measured by mass as per the mix proportions. The fine and coarse aggregates were sampled from large lots by quartering before batching.

Blended cement (given in Table 4.1) to sand ratio of 1:3, and water to cement ratio of 0.5 were used to prepare all mortar samples. The materials for each mortar sample were mixed separately. The blended cement was mixed with the measured quantity of sand. Afterwards, the quantity of water needed was added and mixed for about 4 minutes. The mortar was tamped in the moulds and then vibrated for 2 minutes. After gauging, the mould was covered with a metal plate and a damp hessian sack. For the concrete test, 1:2:4 cement, fine and coarse aggregate ratio, and water to cement ratio of 0.6 were used to produce the concrete samples. In all, the test samples included 75mm cement mortar cubes, 100mm concrete cubes and 150mm x 310mm concrete cylindrical specimens were prepared for the compressive tests. 50mm x 50mm x 150mm concrete prisms were prepared for flexural tensile tests using BS and EN specifications. All the experiments were done at a room temperature of approximately $27^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and $70\% \pm 2\%$ relative humidity. The mortar cubes, concrete cubes and prisms were removed from their moulds 24 hours after gauging and weighed. The weighed cubes were then immersed in a pond of water of average temperature of $22^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and kept for the specified testing periods.

In all, 1075 mortar and 620 samples were prepared for the compressive tests, and 510 mortar samples for the durability. Five samples were tested for each age date.

In all, 1075 mortar and 620 samples were prepared for the compressive tests, and 510 mortar samples for the durability. Five samples were tested for each age date.

4.5.1.2 Slump Test

This test was used to determine the workability of the fresh concrete. The steel mould for the slump test was a frustum of a cone, 300mm high. The mould was thoroughly cleaned and placed on a smooth levelled surface with an opening of diameter 100mm at the top and 200mm at the bottom. It was firmly held against its base and filled with concrete in three layers. Each layer was tamped 25 times with a standard 16mm diameter steel rod that was rounded at the end. The excess concrete was struck off the top and the base was cleared of all droppings. The cone was steadily lifted vertically. A straight edge was placed on top of the inverted empty cone placed alongside the slumped concrete. The slump was measured as the difference between the highest point of the slumped concrete and the underside of the straight edge.

4.5.1.3 Strength tests

The cement mortar and concrete cube and cylindrical specimens were tested for their compressive strengths at 2, 7, 28, 90 and 365 days using a universal testing machine in accordance with EN 197-2 (2000). The flexural tensile strengths of the concretes from the cement blends were determined from the prisms prepared. The modulus of rupture was calculated based on the of elastic theory using the formula:

$$F_{pc} = \frac{PL}{bd^2} \quad 4.5$$

Where F_{pc} = modulus of rupture in N/mm^2 ; P = load (force); L = effective span; b = width of the beam; and d = thickness

4.5.1.4 Water Absorption

The water absorption of the cement mortar cubes, concrete cubes and prisms was determined by weighing the cubes immediately after removing them from their moulds to give the initial mass, m_1 . The cubes were then immersed in water for 28 days. The mass of the wet cubes, m_2 , were then taken before their compressive strengths were tested. The water absorption, w , of the cubes was calculated as;

$$w = \frac{m_2 - m_1}{m_1} \times 100\% \quad 4.7$$

4.6 Durability Tests

Durability of cements and their products refers to their ability to withstand extreme or excessive deleterious conditions which otherwise will affect their required structural performance and resilience. The long-term durability of cementitious materials is mostly dependent upon their physical and chemical properties. It is recognized that the more important prerequisite is reducing the permeability of material to the ionic species. C_3A -related compounds are given much attention when it comes to cement durability because sulfate resistance and the chloride binding capacity of cement products depend on the stability of C_3A hydrates formed before the attack (Bonavettiet *al*, 2001). In sulfate attack, ettringite formed prior to the immersion in sulfate solution will be a stable phase while the monosulfoaluminate and the monocarboaluminate will be unstable phases.

4.6.1 Sulphate and Chloride Resisting Tests

Cement products, especially concretes and mortars, are attacked by acidic media, and are severely affected by sulphates and chlorides which are found in the soil and/or groundwater. These acids affect the cement structures negatively through chemical actions leading to expansion and corrosion of reinforced steel that eventually result

in loss of strength and durability. It is therefore essential to determine the performance of cements in these acidic media so as to determine their durability (O'Farrel, *et al*, 1999, Osborne, 1999).

Cement mortar cubes produced as in 4.51.1 – 4.51.3 were immersed in 5% Na₂SO₄ solutions and sea water for 28, 90 and 365 days. The cubes were examined visually, photographed and their compressive strengths determined.

4.6.2 Strength Deterioration Factor (SDF)

The deterioration of the mortar cubes was investigated by determining the strength deterioration factor due to the sulphate and chloride attack was determined using the formula by Murthi and Sivakumar (2008):

$$SDF = \frac{(f_{cw} - f_{ca})}{f_{cw}} \quad 4.7$$

where f_{cw} = the average compressive strength of cubes in water

f_{ca} = the average compressive strength of cubes in acidic solution

The cubes were tested for compressive strength at 28, 180 and 365 days according to EN 196-2 (2000).

CHAPTER FIVE

EXPERIMENTAL RESULTS

5.1 Physical Properties

5.1.1 Constituent materials

The physical properties of the ordinary Portland cement (as reference material), admixtures (limestone, clam shell, Pozzolana and steel slag), sand and crushed aggregates such as colour, moisture content, specific gravity, and their particle size distribution were determined. These are presented in Table 5.1. The particle size distribution curves of the sand according to hydrometer method and sieve analysis of material retained on the 75 μ m sieve are given in Figs. 5.1 and 5.2 respectively whilst that of the admixtures are shown in Fig. 5.3. A detailed sieve analysis of the sand fraction retained on 75 μ m and crushed aggregates are shown in Table 5.2.

Table 5.1: Physical Properties of Materials

	Reference		Clam	Steel	Mankranso	Pozzolana
Property	Cement	Limestone	shells	slag	clay	
Colour	Grey	grey	white	deep grey	yellow	Red
Specific gravity	3.16	2.76	2.82	2.85	2.64	2.59
Particle size (mm) of milled admixtures, %						
<0.002		-	-	-	32	35
0.002 - 0.06		76	85	30	30	62
0.05 - 0.6		20	14	70	38	3

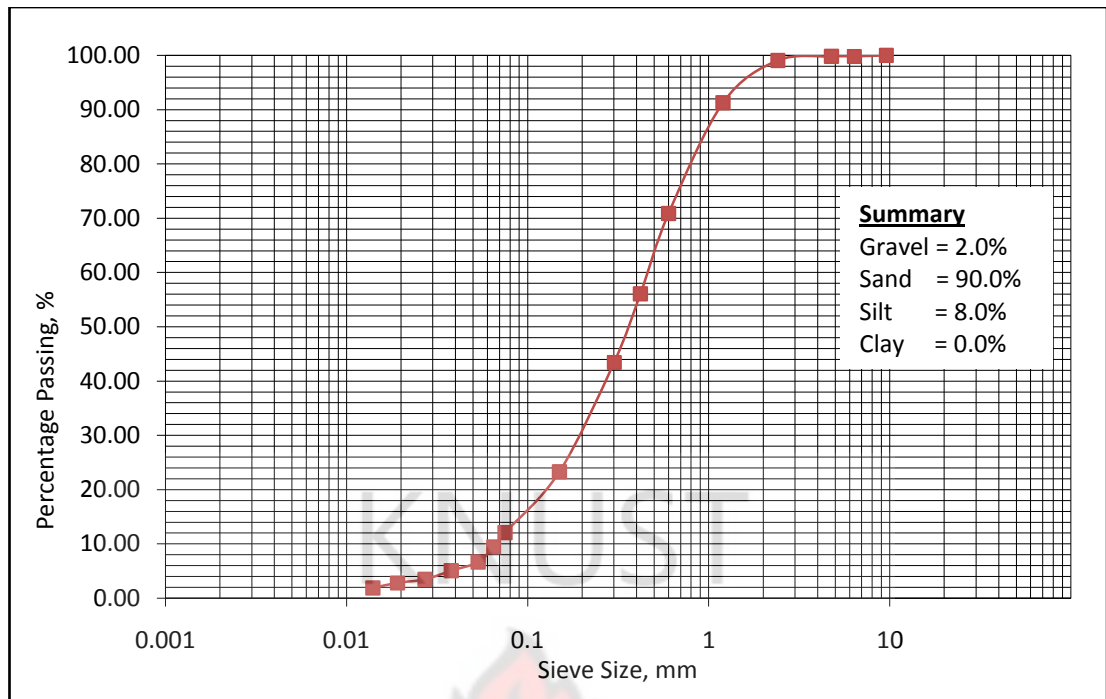


Figure 5.1: Particle size distribution of sand by hydrometer method

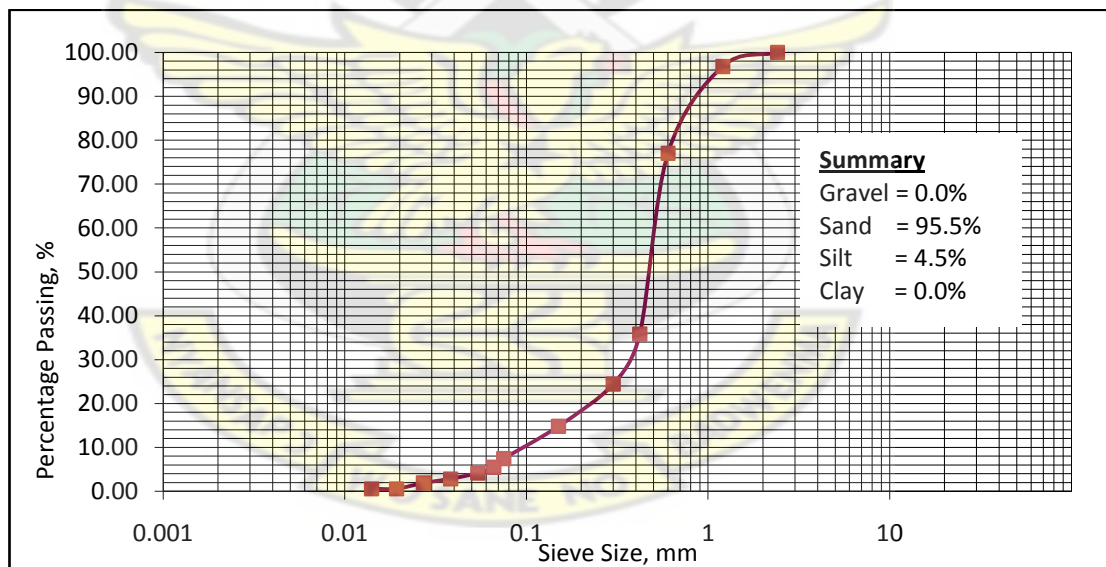


Figure 5.2: Particle size distribution of sieved sand

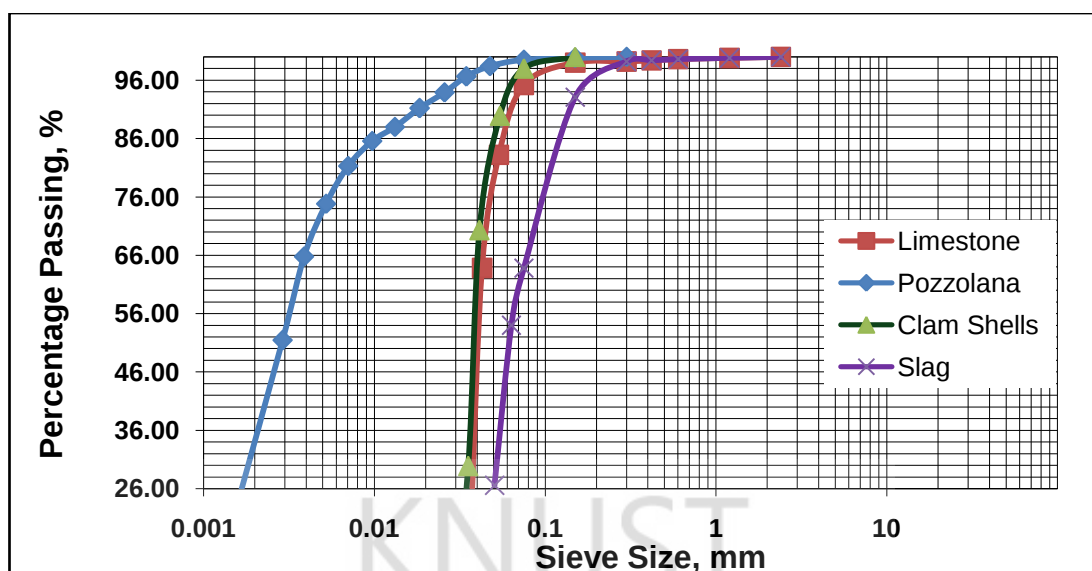


Figure 5.3: Particle size distribution of admixtures

Table 5.2: Sieve analysis of sand and crushed aggregates

Sieve size, Mm	% Passing			
	Sand	BS 882 Limits	Crushed aggregates	BS 882 limits (20mm – 5mm)
37.5	-		100.00	100
25.4	-		100.00	
20.0	-		98.00	90 - 100
19.0	-		98.73	
12.7	-		33.66	
10.0	-		14.00	30 – 60
9.5	-		14.21	
5.0	100.00	89- 100	0.50	0 – 10
4.76	99.83		0.24	
2.36	98.13	65 – 100	0.10	-
1.18	84.33	45 – 100	-	
0.60	61.33	25 – 80	-	
0.42	47.73		-	
0.30	37.73	5 – 48	-	
0.15	23.53	0 – 15	-	
0.08	12.53		-	
0.065	10.15		-	
0.05	8.00		-	
0.038	5.42		-	
0.025	3.85		-	
0.02	2.27		-	
0.014	0.69		-	

5.1.2 Cement samples

The physical properties of the various cement blends determined include the specific gravity, consistency, setting times (initial and final), soundness (expansion) and water permeability. The Blaine values of the blended cements, which ranged from 408 to 525m²/kg are given in Table 5.3. The results obtained for specific gravity and expansion of the cement samples as well as the water demand and setting times of cement pastes are shown in Table 5.4. The water permeability properties of some selected cement samples are presented in Table 5.5.

Table 5.3: Blaine fineness of reference and blended cements

Sample	Symbol	Fineness (m ² /kg)
Reference cement	Rh	340
5%Slag cement	5S	408
5%Shell cement	5Sh	431
5%Limestone cement	5L	438
5%Pozzolana cement	5P	510
5%Shell 5%slag cement	5Sh5S	410
5%Pozzolana 5%slag cement	5P5S	496
5%limestone 5%slagcement	5L5S	410
5%Pozzolana 5%shell cement	5P5Sh	516
5%Limestone 5%shell cement	5L5Sh	440
5%Pozzolana 5%limestone cement	5P5L	525

Table 5.4: Expansion and shrinkage values of reference and blended cements

Sample	Water demand, %	Setting time, min		Specific gravity	Expansion, Mm
		Initial	Final		
Rh	26.0	120	210	3.16	1.2
5S	24.5	91	146	3.03	1.4
5Sh	26.6	90	150	2.92	0.8
5P	26.8	95	154	2.97	0.7
5L	26.0	85	153	2.92	1.4
5Sh5S	25.6	106	162	3.08	1.5
5P5S	26.4	104	160	2.92	1.4
5L5S	26.2	106	159	2.92	1.2
5L5Sh	26.0	96	159	2.98	1.1
5P5Sh	24.8	98	174	2.93	1.5
5P5L	28.0	106	161	2.93	1.8
10L5P	32.8	157	217	3.02	1.0
10Sh5S	31.8	165	245	2.82	1.3
10S5Sh	31.6	164	242	2.84	1.2
10L5S	31.2	162	234	2.89	1.2
10S5L	31.3	160	242	2.93	1.1
10P5S	32.0	158	246	3.10	1.4
10S5P	31.8	154	243	3.09	1.6
10Sh5L	30.5	96	229	2.95	1.2
10L5Sh	30.4	92	231	2.96	1.1
10P10S	34.2	170	257	3.11	0.8
10L10S	30.6	163	242	3.03	0.6
10L10Sh	31.4	159	262	2.93	0.9
10P10Sh	30.0	126	252	3.03	0.7
10L10P	30.0	121	241	2.98	1.2
5P5Sh5S	32.0	113	209	3.03	1.0
5L5Sh5S	30.4	116	185	2.89	1.4
5L5P5S	32.0	140	203	3.10	1.1
5L5P5Sh	30.0	109	220	2.96	1.1
2.5P2.5S2.5Sh	30.0	109	180	2.73	1.2
2.5L2.5P2.5Sh	30.4	112	216	2.86	1.1
2.5P2.5L2.5S	30.0	113	185	2.87	1.1
2.5P2.5L2.5Sh	30.2	118	203	2.77	1.2
2.5P2.5S2.5L2.5Sh	30.0	151	248	2.98	1.4
5P5S5L5Sh	30.2	115	210	3.10	1.3

Table 5.5: Water permeability of cement concretes

Material	Water permeability(K_a) $\times 10^{-4}$
Reference cement	4.42
5Slag cement	4.48
5% Shells cement	3.87
5% Limestone cement	3.90
5% Pozzolana cement	3.39
5%Pozzolana5%shell5%slag cement	4.03
5% Limestone5%Slag5%Shell cement	4.24
5%Pozzolana5%limestone5%slag cement	4.18
5%Pozzolana5%limestone5%shell cement	3.98
2.5%Pozzolana2.5%limestone2.5%Shell2.5%slag cement	4.52

5.2 Chemical properties of cement samples

The chemical compositions of the four admixtures, calcined clay samples (pozzolana), ordinary Portland (reference) and the blended cements were determined by X-ray fluorescence (XRF). The results of the chemical analysis of the blended cements; namely, 5% x and 5% x 5% y cements, are shown in Table 5.6. Table 5.7 presents the chemical compositions of 10% x 5% y and 5% x 5% y 5% z cement respectively whilst Table 5.8 gives that of 10% x 10% y ,2.5% x 2.5% y 2.5% z 2.5% p and 5% x 5% y 5% z 5% p blended cements respectively, where x,y,z,p represent slag, shell, limestone and pozzolana.

Table 5.6: Chemical composition of 5%*x* and 5%*x*5%*y* blended cements

Chemical compound %	Reference cement	% mass									
		5%Slag		5%Pozzolana		5%Shells		5%Limestone		5% Pozzolana	
		Cement		cement		cement		Cement		cement	
SiO ₂	18.80	19.94		25.15		18.49		17.51		23.57	
Fe ₂ O ₃	3.57	4.85		3.62		3.14		3.11		4.91	
Al ₂ O ₃	4.36	3.32		6.09		3.20		5.53		3.46	
CaO	1.89	56.41		53.54		57.38		55.51		55.02	
MgO	57.04	2.89		1.27		1.63		2.27		2.49	
Na ₂ O	4.78	1.7		0.46		1.00		1.56		2.1	
K ₂ O	4.43	4.21		3.87		7.59		5.47		5.25	
P ₂ O ₅	0.14	0.18		1.24		0.09		1.48		0.08	
Cl	0.16	0.1		0.1		0.0		0.1		0.05	
TiO ₂	0.22	0.05		0.05		0.07		0.24		0.05	
MnO	0.01	0.37		0.05		0.05		0.04		0.4	
SO ₃	0.85	1.94		1.83		1.7		1.64		1.63	
L.O.I*	3.60	2.0		1.0		7.5		4.0		3.5	
Al ₂ O ₃	0.68	1.68		1.019		1.78		0.7		1.55	
Fe ₂ O ₃											

- - Loss on ignition; *xy* - represent admixtures

Table 5.7: Chemical composition of 10%*x*5%*y* and 5%*x*5%*y*5%*z* blended cements

% by mass											
Ternary blend								Quaternary blend			
Chemical compound, %	Reference cement	10% Pozzoana 5% Slag Cement	10% Slag 5% shell Cement	10% Pozzolana 5% shell Cement	10% Limestone 5% shell Cement	10% Slag 5% limestone Cement	10% Pozzolana 5% limestone Cement	5% Pozzolana 5% shell 5% slag Cement	5% Limestone 5% shell 5% slag Cement	5% Limestone 5% pozzolana 5% slag Cement	5% Limestone 5% Pozzolana 5% shell Cement
SiO ₂	18.80	18.12	14.76	23.64	15.51	15.37	21.58	18.28	13.95	18.41	19.52
Fe ₂ O ₃	3.57	5.71	5.70	3.54	2.65	5.65	3.45	4.30	2.70	4.57	3.04
Al ₂ O ₃	4.36	3.08	3.76	2.30	5.62	3.04	4.83	3.06	2.92	6.18	3.06
CaO	1.89	49.43	52.40	48.51	52.69	52.38	47.50	50.24	54.69	48.33	53.57
MgO	57.04	0.60	0.75	7.32	2.89	0.56	6.30	2.23	3.21	3.06	2.57
Na ₂ O	4.78	1.30	5.10	1.20	1.96	11.20	1.20	1.00	1.00	3.80	5.80
K ₂ O	4.43	9.51	8.50	8.70	6.40	10.14	8.84	7.63	7.58	6.57	9.05
P ₂ O ₅	0.14	0.11	0.55	0.12	1.88	0.10	1.14	0.59	0.88	1.54	0.10
Cl	0.16	0.01	0.01	0.01	0.07	0.01	0.01	0.01	0.01	0.03	0.01
TiO ₂	0.22	0.09	0.08	0.08	0.07	0.10	0.08	0.06	0.07	0.06	0.08
MnO	0.01	0.73	0.67	0.09	0.06	0.65	0.08	0.31	0.05	0.36	0.08
SO ₃	0.85	3.95	4.06	3.81	3.67	3.97	3.55	3.87	3.96	3.64	3.86
L.O.I	3.60	10.00	4.00	1.00	6.00	0.50	1.00	9.00	8.00	4.00	2.00

* - Loss on ignition

xyz - represent admixtures

Table 5.8: Chemical composition of 10%x10%y,2.5%x2.5%y2.5%zx2.5%p and 5%x5%y5%z5%p blended cements

Oxide Composition	% by Mass								Reference cement
	10%Shell 10%slag Cement	10%Pozzolana 10%shell Cement	10%Pozzolana 10%slag Cement	10%Limestone 10%slag Cement	10%Limestone 10%shell Cement	10%Pozzolana 10%limestone Cement	5%Pozzolana 5%limestone 5%slag 5%shell Cement	2.5%Pozzolana 2.5%limestone 2.5%slag 2.5%shell Cement	
SiO ₂	16.76	24.04	25.61	18.01	17.03	23.38	23.08	19.14	18.80
Fe ₂ O ₃	5.21	3.15	6.44	5.94	2.39	3.12	4.35	3.51	3.36
Al ₂ O ₃	2.14	5.47	5.95	2.17	1.86	5.75	4.67	2.85	3.57
CaO	49.21	46.27	43.67	50.92	52.06	47.90	54.78	51.33	57.04
MgO	2.13	1.90	2.32	2.72	2.25	2.19	2.76	2.25	1.89
Na ₂ O	1.51	2.26	2.64	2.38	1.35	2.56	3.60	2.22	4.70
K ₂ O	1.55	1.73	1.64	1.61	1.63	2.41	1.91	1.94	4.43
P ₂ O ₅	0.25	0.35	0.37	0.12	0.16	0.28	0.15	0.25	0.22
Cl	0.01	0.02	0.01	0.01	0.01	0.01	0.00	0.01	0.01
TiO ₂	0.18	0.38	0.44	0.19	0.14	0.34	0.27	0.18	0.14
MnO	0.60	0.07	0.65	0.70	0.05	0.06	0.35	0.20	0.14
SO ₃	4.00	3.66	3.98	4.30	3.75	3.83	3.81	4.33	0.85
L.O.I	17.00	10.00	7.00	11.00	17.00	8.00	0.10	11.00	3.00

* - Loss on ignition

xyzp - represent admixtures

5.3: Mineralogical properties of cement samples

5.3.1 Infrared spectrometry

The infrared spectra of the various blended cements are given in Figs 5.4 – 5.6. The results of the analysis are given in Tables 5.9 – 5.10.

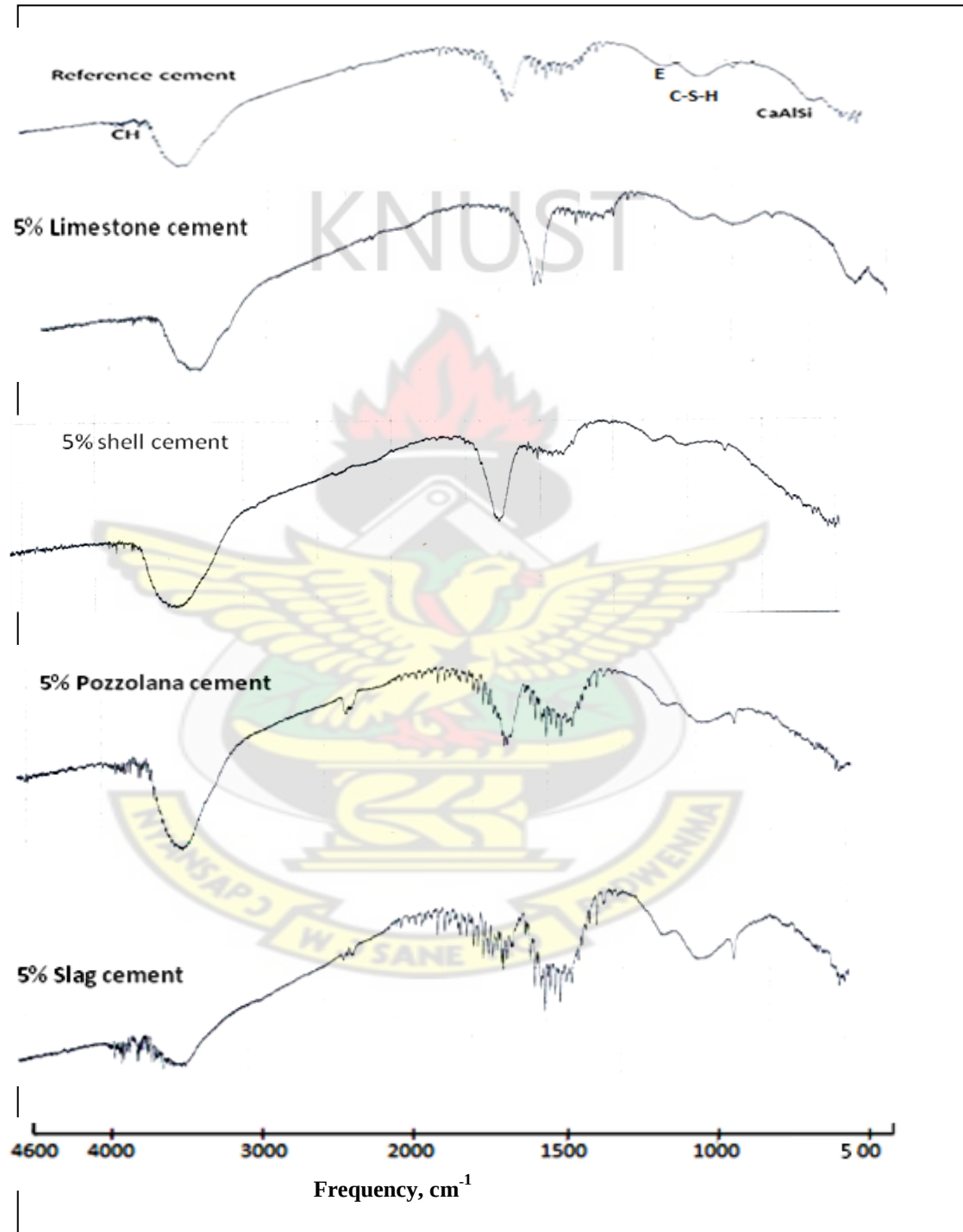


Figure 5.4: Infrared spectra of reference and binary blended cement at 7 days

E= ettringite; *CH*= $\text{Ca}(\text{OH})_2$; *C-S-H*= Calcium silicate hydrate; *CaAlSi* = Calcium Aluminosilicate hydrate

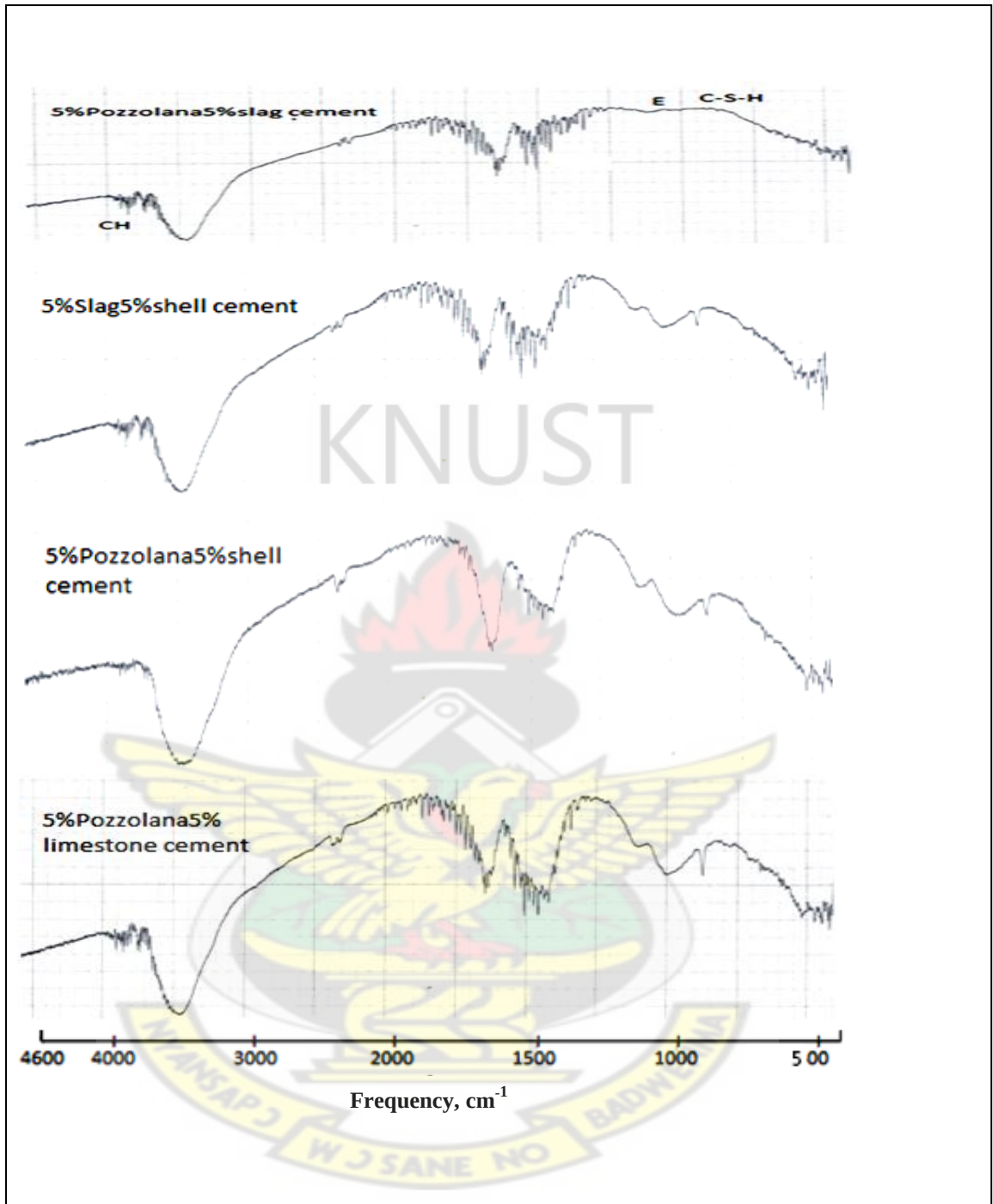


Figure 5.5: Infrared spectra of reference and binary blended cement at 7 days

E= ettringite; CH= $\text{Ca}(\text{OH})_2$; C-S-H= Calcium silicate hydrate;; CaAlSi = Calcium Aluminosilicate hydrate

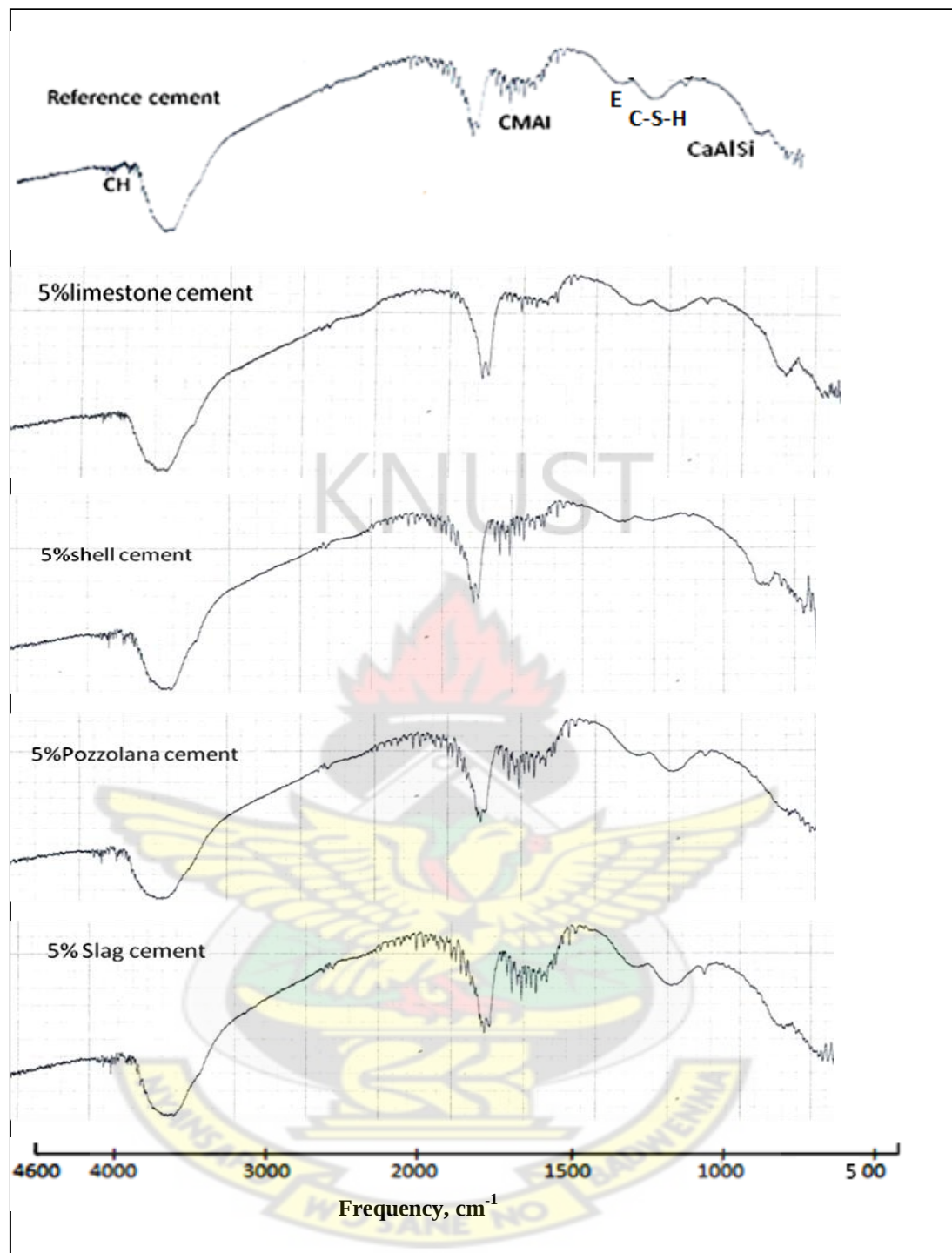


Figure 5.6: Infrared spectra of reference and binary blended cement at 28 days

E= ettringite; CH= $\text{Ca}(\text{OH})_2$; C-S-H= Calcium silicate hydrate; CaAlSi = Calcium Aluminosilicate hydrate

Table 5.9: IR vibrations of the principal bands of hydrated samples.

Frequency (cm ⁻¹)										Assignment/Vibration
7 days	28 days	7 days	28 days	7 days	28 days	7 days	28 days	7 days	28 days	
Reference cement		5% Limestone cement		5% Shell cement		5% Pozzolana cement		5% Slag cement		
3645	3645	3645	3645	3645	3645	3645	3645	3645	3845	stretching O-H of Ca(OH) ₂
3450	3450	3475	3460	3475	3450	3480	3450	3500	3475	symmetric and asymmetric stretching of (v ₁ & v ₃)O-H of water
1650	1645	1650	1650	1650	1650	1650	1650	1650	1650	Deformation of v ₂ H-O-H
1480	1480	1480	1480	1480	1480	1480	1480	1480	1480	v ₃ CO ₃ ²⁻
1120	1120	1120	1120	1120	1120	1120	1120	1120	1120	Ettringite
1100	1100	1100	1100	1100	1100	1100	1100	1100	1100	v ₃ SO ₄ ²⁻
970	970	970	970	970	970	970	970	970	970	v ₃ SiO ₄ ⁴⁻ ; C-S-H
875	875	875	875	875	875	875	875	875	875	v ₂ CO ₃ ²⁻
-	-	625	-	-	-	665	-	-	-	v ₄ SiO ₄
600	600	600	600	-	-	-	-	600	600	v ₄ SiO ₄
-	-	518	518	518	518	518	518	518	518	v ₄ SiO ₄
462	462	462	-	462	462	462	462	-	462	v ₂ SiO ₄ , CaAlSi hydrate
-	-	-	450	-	-	-	-	450	-	v ₂ Si-O

Table 5.10: IR vibrations of the principal bands of hydrated samples

Vibration	Wave number (cm ⁻¹)											
	5% Pozzolana 5% limestone cement		5%shell 5%Slag cement		5%limestone 5%Slag cement		5%Pozzolana 5%slag Cement		5%limestone 5%Shell cement		Reference cement	
	7 days	28 days	7 days	28 days	7 days	28 days	7 days	28 days	7 days	28 days	7 days	28 days
v ₂ H ₂ O	1650	1640	1650	1640	1640	1640	1650	1650	1650	1640	1650	1640
v ₃ CO ₃	1450	1450	1450	1400	1455	1440	1480	1510	1480	1510	1500	1500
v ₃ SiO ₄	975	970	970	980	960	970	-	970	-	970	960	970
v ₂ CO ₃	875	875	875	870	875	875	880	875	875	875	875	875
v ₄ CO ₃	715	-	-	-	-	-	-	-	-	-	-	-
v ₄ SiO ₄	520	525	520	520	620	620	520	540	595	620	550	600
v ₄ SiO ₄	480	490	475	465	470	475	465	500	465	470	510	500
v ₂ SiO ₄	450	460	450	450	450	450	445	445	450	460	450	450

5.3.2 X-ray diffractometry

The X-ray diffraction graphs of hydrated Portland and blended cements samples at 28 days are given in Figures 5.7 and 5.8. Appendix I gives the detailed spectra of some of the cement samples.

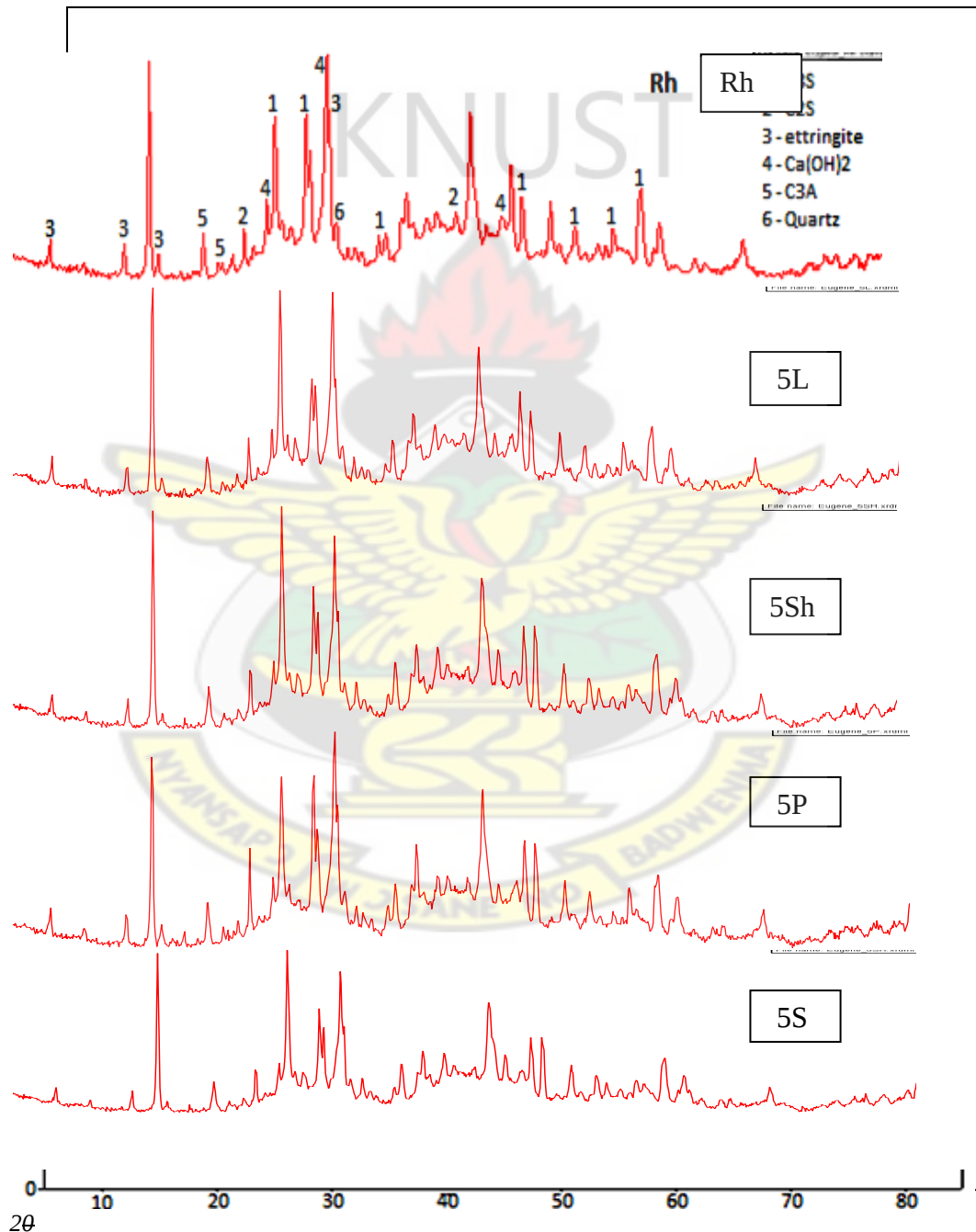


Figure 5.7: X-ray diffraction graphs of reference and blended cements at 28 days

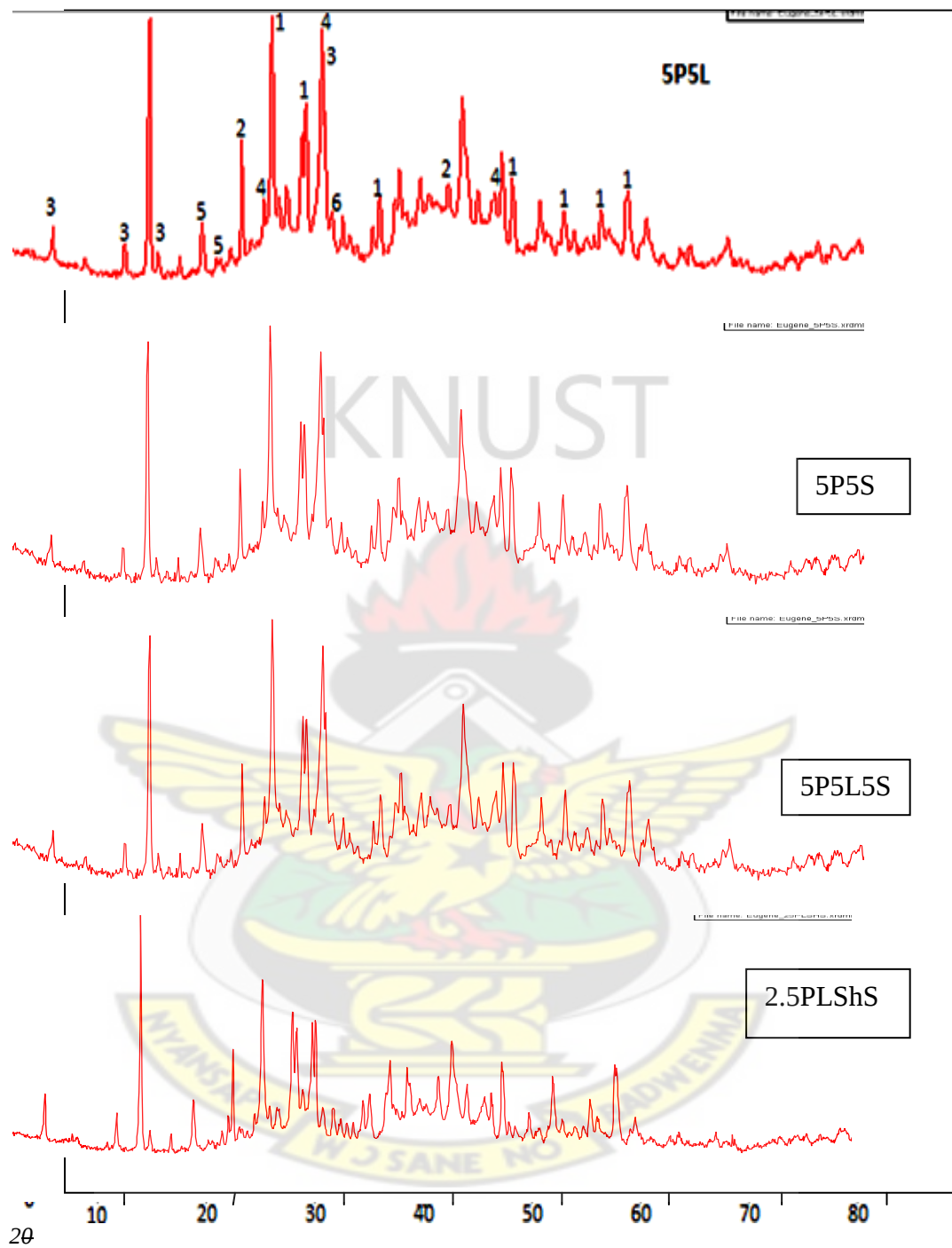


Figure 5.8: X-ray diffraction graphs of reference and blended cements at 28 days

The percentage compositions of ettringite and portlandite of the resolved XRD graphs (Sample in Appendix I) of the cement samples were calculated using Equation 5.1 (Bishop, 1989). The results are presented in Table 5.11 and detailed example is given in Appendix II.

$$C_A = 100 \times \frac{\left(\frac{I_A}{F_A} \right)}{\sum_i \left(\frac{I_i}{F_i} \right)} \quad 5.1$$

C_A = % Composition of mineral A, I_A = Peak Area of mineral A, F_A = Response factor of sample A, I_i = Peak area of other mineral and F_i = Response factor to the other minerals

Table 5.11: Percentage Composition of ettringite and portlandite from resolved XRD graph

Sample	2θ	R _F	Area	Normalised Area*	% Composition	
					Ettringite	Portlandite
Rh	29	0.220	3256	716	9.1	-
	51	1.141	2534	2891	-	36.9
5L	31	0.202	13131	2652	35.3	-
	55	1.044	960	1002	-	13.4
5SH	29	0.184	14149	2603	15.5	-
	51	0.951	1392	1324	-	7.9
5P	27	0.253	12235	2471	33.2	-
	50	1.095	909	949	-	12.7
5P5L	24	0.197	2961	583	6.5	-
	54	0.996	810	807	-	8.8
5P5S	28	0.220	13020	2864	21.7	-
	51	0.993	1204	1196	-	9.1
5P5L5S	74	0.616	-	-	1.8	-
	69	0.339	1103	1265	-	10.14
2.5PLShS	72	0.201	-	-	12.85	-
	69	0.490	-	-	-	2.1

*Normalized area – obtained after graph is resolved (Appendix II)

5.4 Microstructure of blended cement pastes

The micrographs of the SEM analysis performed on both the test specimens and hydrated cement samples at 28 days are shown in Figs. 5.9 – 5.14. Figures 5.15-5.17 provide EDX pictorials of some of the blended cement samples.

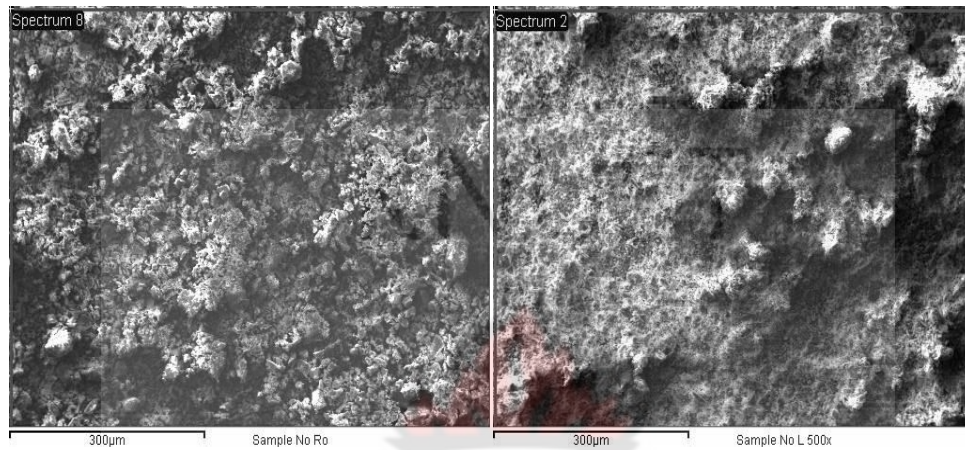


Figure 5.9: Microstructure of (a) portland cement and (b) limestone sample

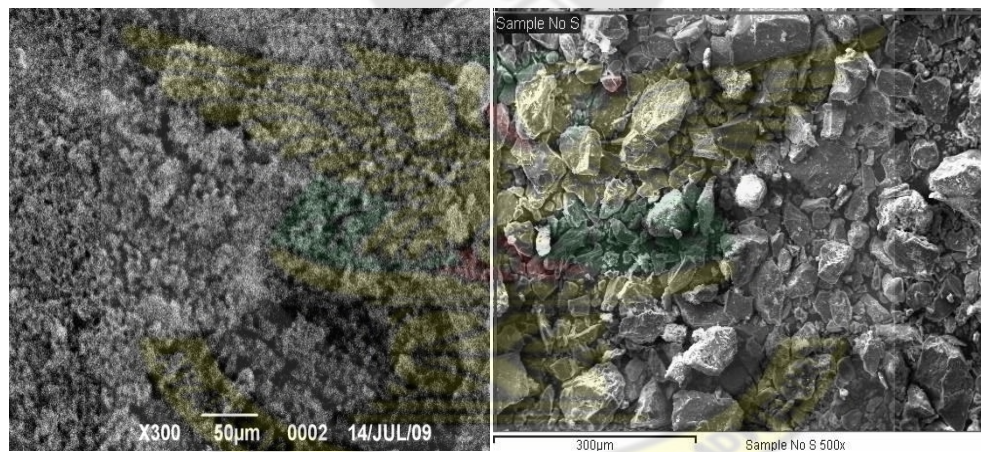


Figure 5.10: Microstructure of (a) clay pozzolana and (b) steel slag sample

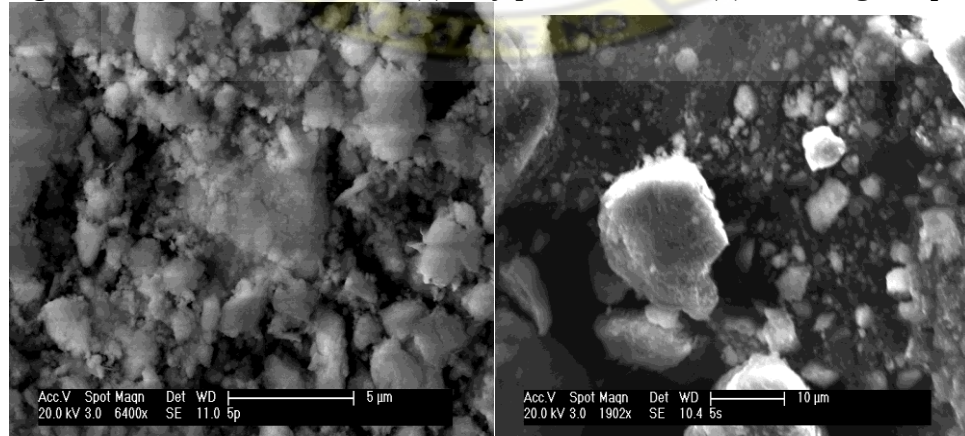


Figure 5.11: Microstructure of (a) 5%pozzolana cement and (b) 5%slag cement

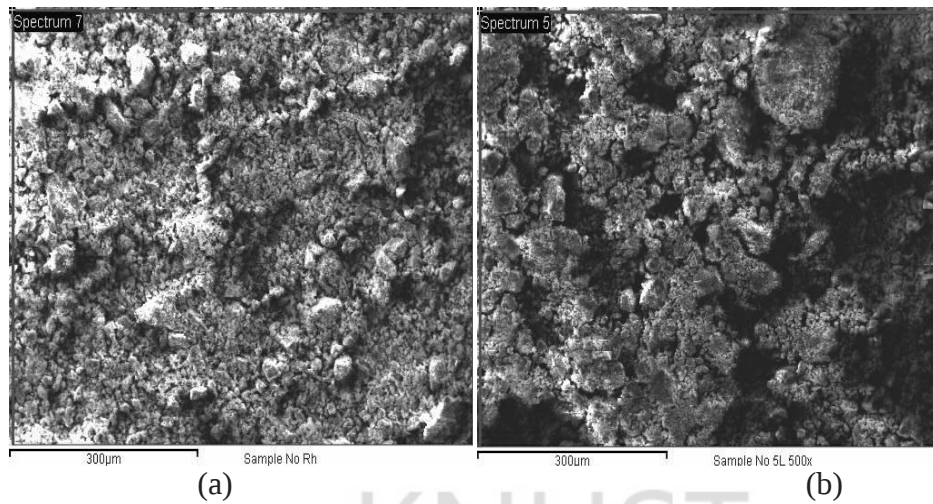


Figure 5.12: Microstructure of (a) portland cement and (b) 5% limestone cement

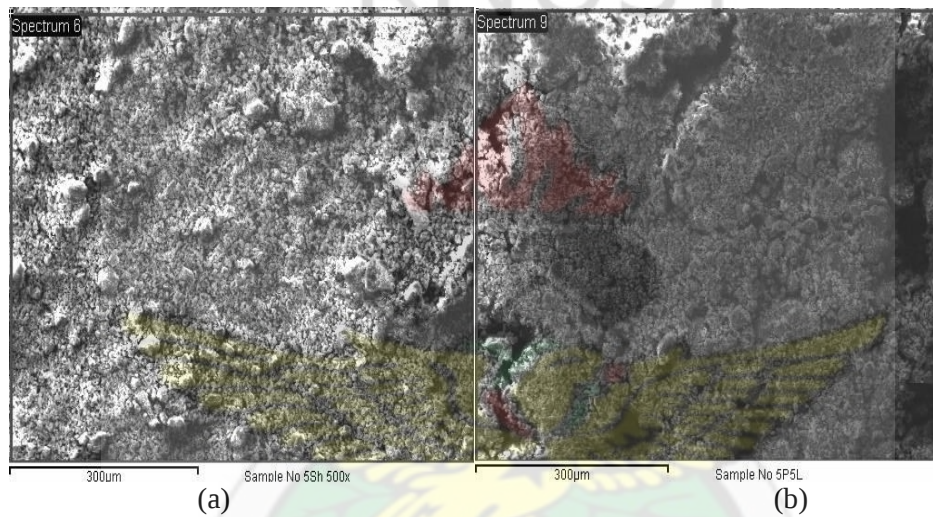


Figure 5.13: Microstructure of (a) 5% shell cement and (b) 5% pozzolana 5% limestone cement

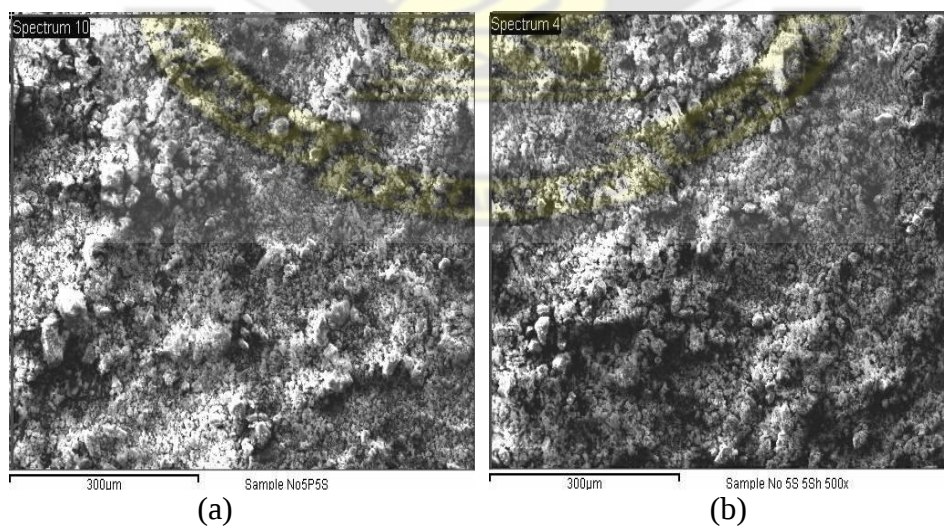


Figure 5.14: Microstructure of (a) 5% pozzolana 5% slag cement and (b) 5% slag 5% shell cement

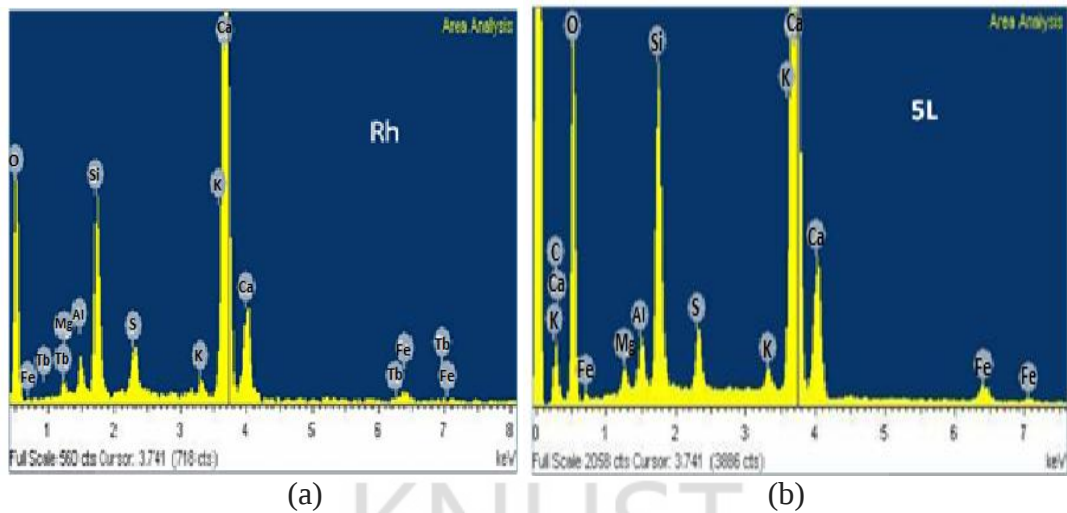


Figure 5.15: EDX of (a) hydrated portland cement and (b) 5%limestone cement

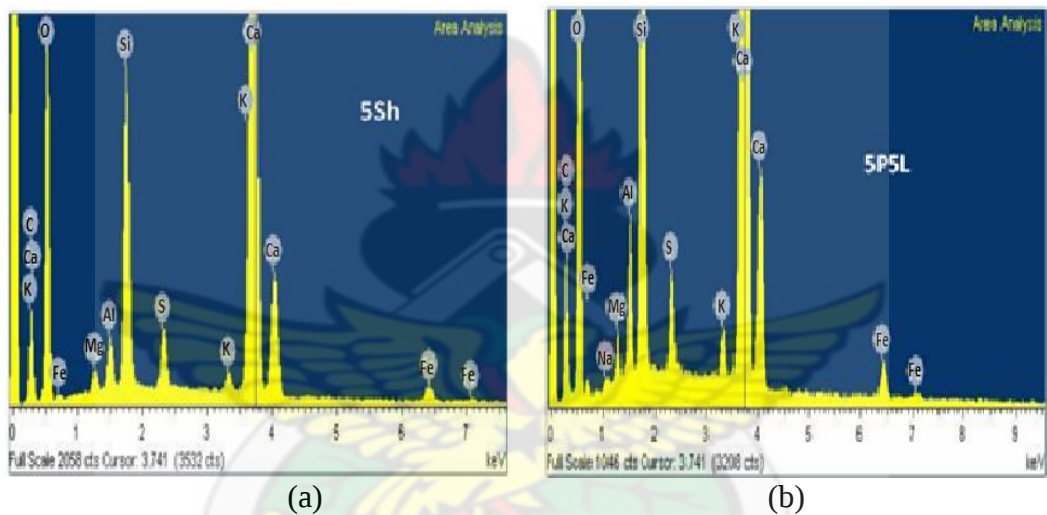


Figure 5.16: EDX of (a) 5%shell cement and (b) 5%pozzolana5%limestone cement

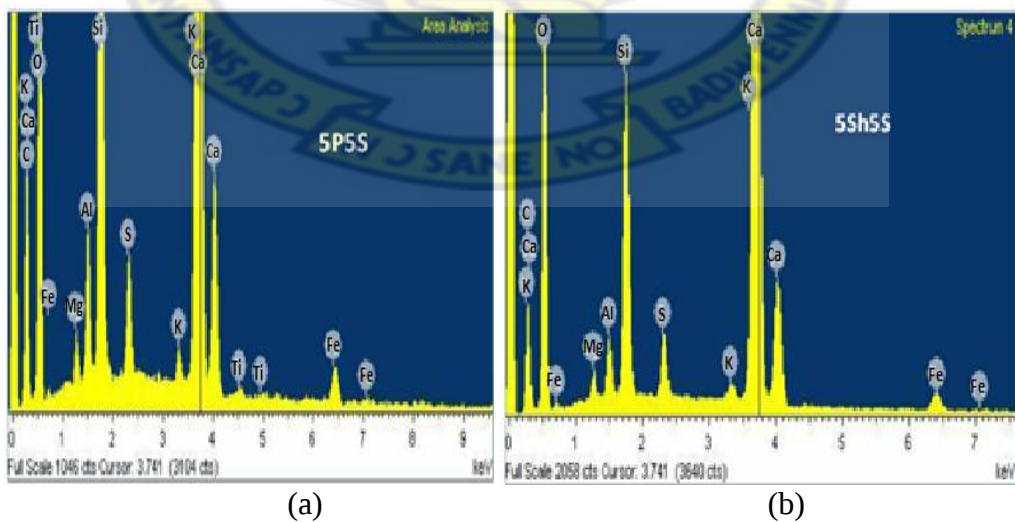


Figure 5.17: EDX of (a) 5%pozzolana5%slag cement and (b) 5%shell5%slag cement

The percentage by mass of the elemental composition generated from the EDX graphs by the equipment software are presented in Table 5.12. Detailed sample of SEM/EDX results are presented in appendix III.

Tab 5.12: Elemental composition of hydrated cements from EDX analysis

Element	Atomic mass	% weight					
		Rh	5Sh	5L	5P5S	5P5L	5S5Sh
C	12	8.67	11.41	6.94	14.14	9.80	13.11
O	16	48.21	49.70	50.80	49.56	50.57	48.62
Na	22	-	-	-	-	0.15	-
Mg	24	0.24	0.57	0.60	0.61	0.62	0.62
Al	26	1.06	0.94	0.98	1.32	1.55	1.04
Si	28	5.52	5.90	5.88	6.02	6.45	5.42
S	32	1.39	1.25	1.27	1.24	1.15	1.25
K	38	0.70	0.50	0.55	0.44	0.70	0.39
Ca	40	32.63	28.51	31.73	25.07	27.52	28.32
Ti	48	-	-	-	0.17	-	-
Fe	56	1.07	1.23	1.24	1.44	1.50	1.24
Tb		0.51	-	-	-	-	-
Total		100.00	100.01	99.99	100.01	100.01	100.01

5.5 Thermal properties of Cement samples

Figures 5.18– 5.25 give the thermograms of the cement samples. They show the phase changes (DTA graphs) that took place and mass losses (TG) when the samples were treated from 25°C to 1000°C.

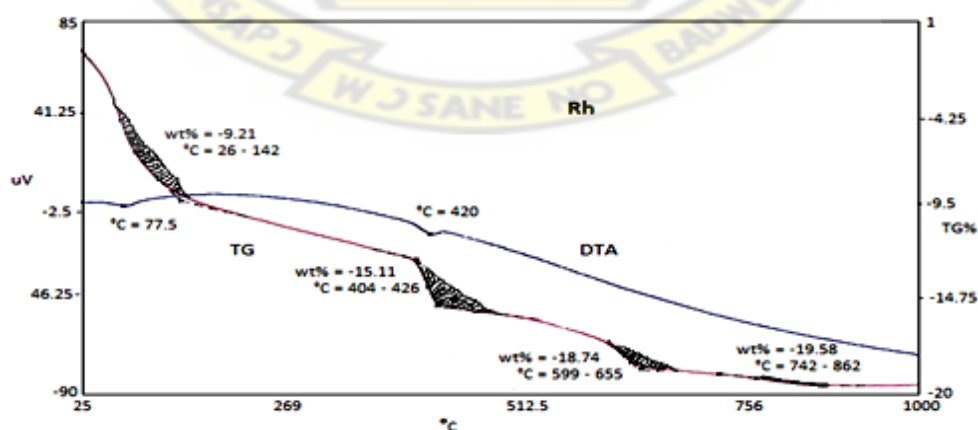


Figure 5.18: Thermograph (TG/DTA) of reference Portland cement

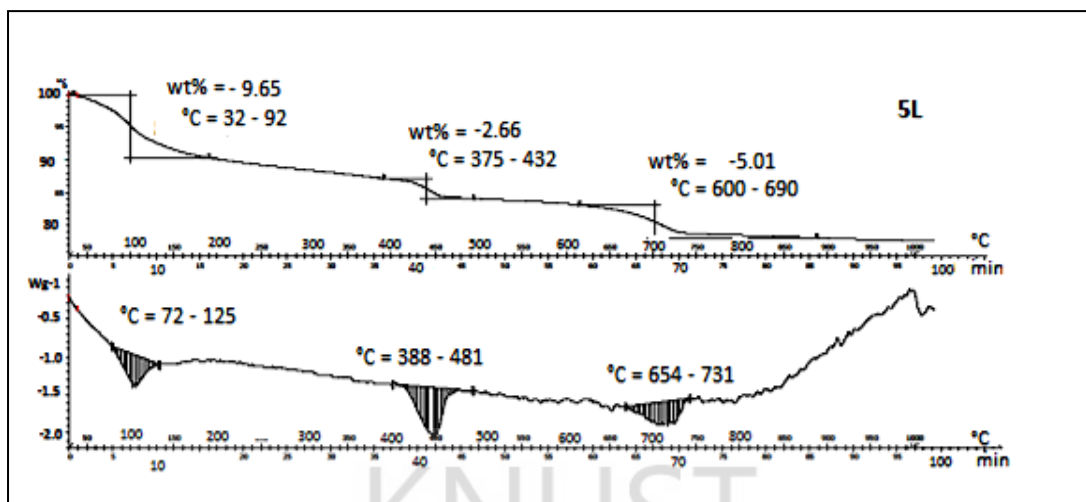


Figure 5.19: Thermograph (TG/DTA) of 5% limestone cement

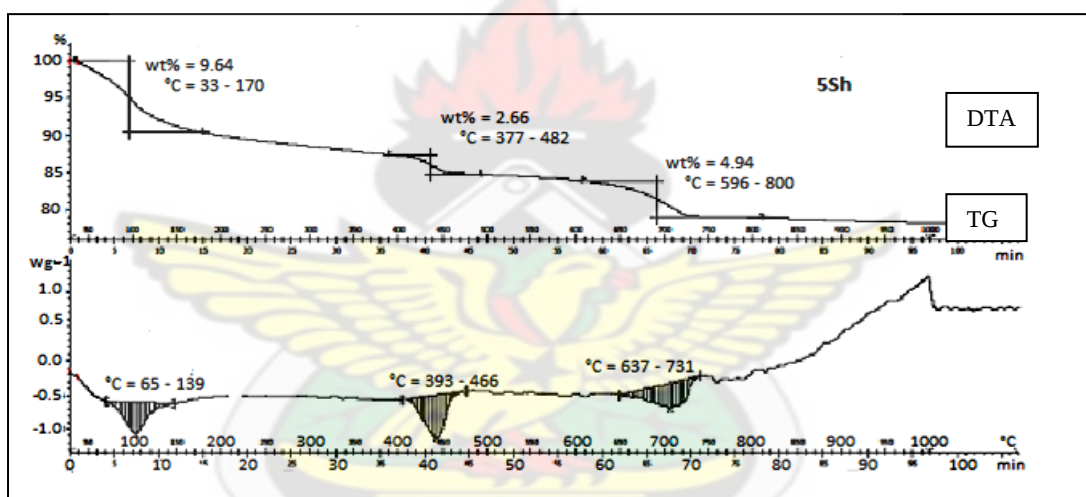


Figure 5.20: Thermograph (TG/DTA) of 5% shell cement

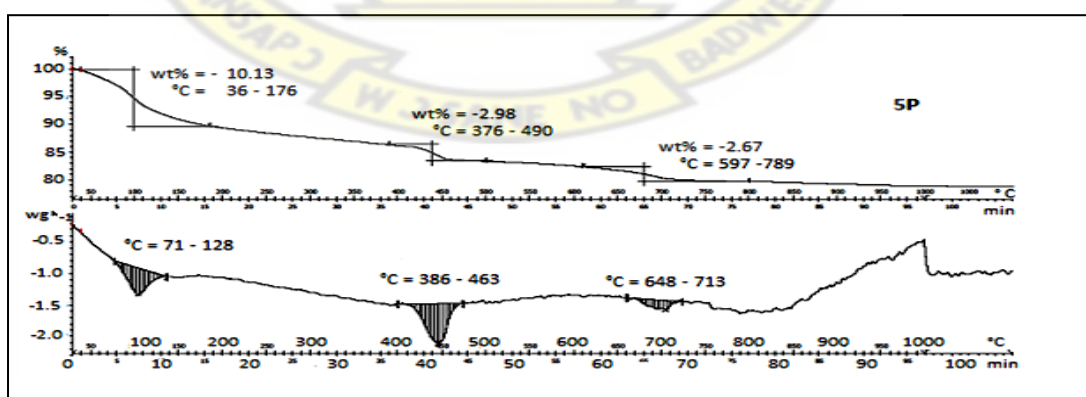


Figure 5.21: Thermograph (TG/DTA) of 5% pozzolana cement

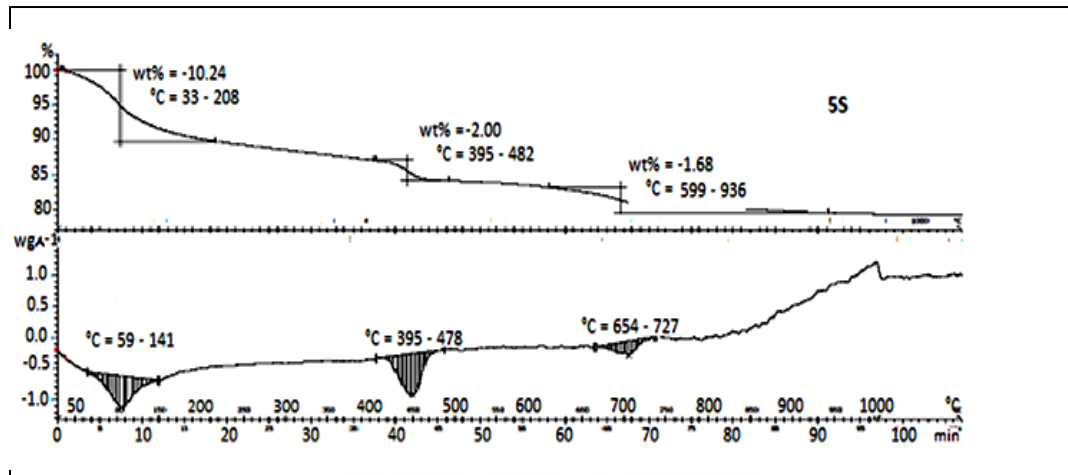


Figure 5.22: Thermograph (TG/DTA) of 5%slag cement

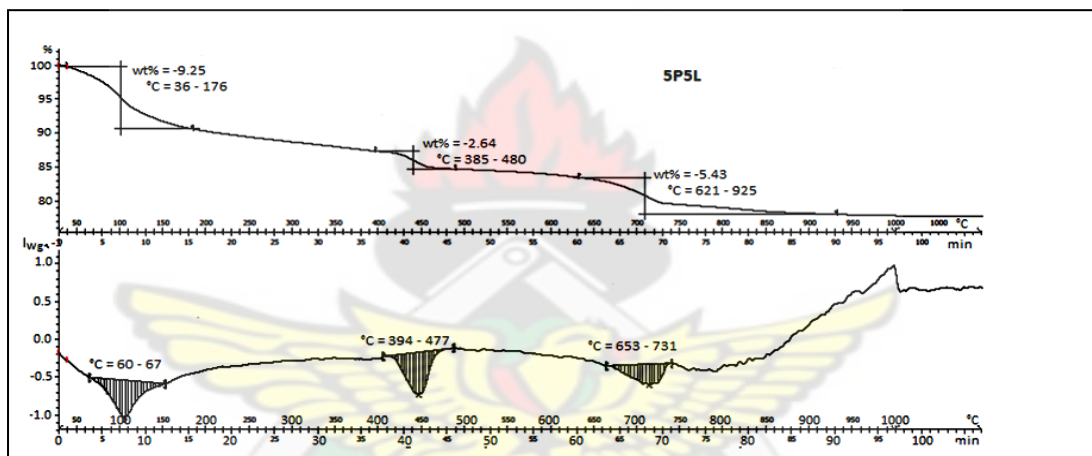


Figure 5.23: Thermograph (TG/DTA) of 5%pozzolana5%limestone cement

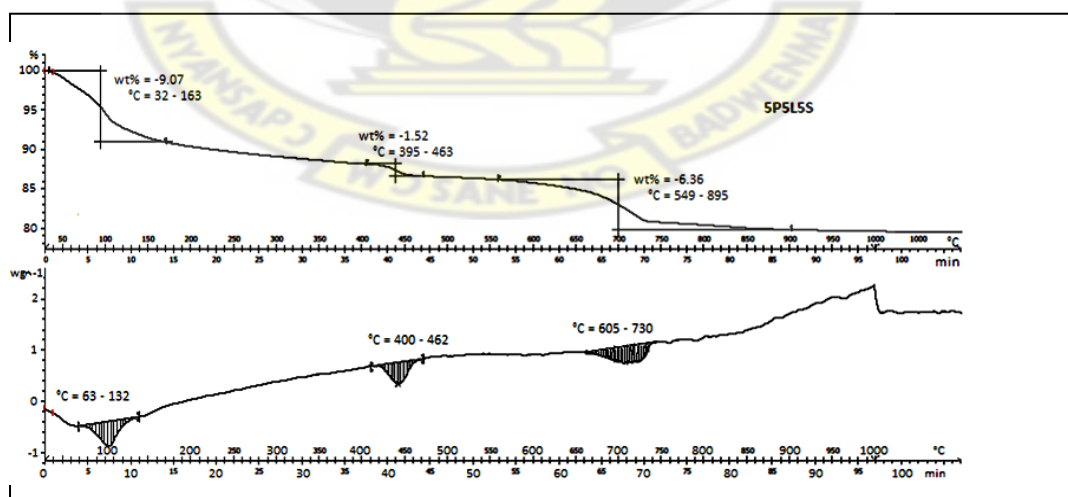


Figure 5.24: Thermograph (TG/DTA) of 5%pozzolana5%limestone5%slag cement

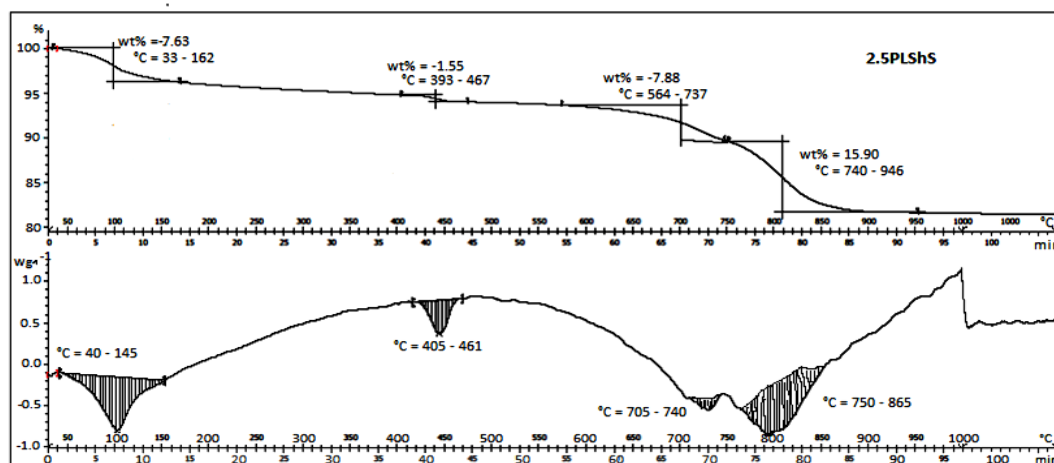


Figure 5.25: Thermograph (TG/DTA) of blended cement containing 2.5% each of pozzolana, limestone, shell and slag

Based on the loss of mass (TG) during the test as a result of the phase changes (DTA), estimated percentage mass of portlandite in the cement samples was calculated and presented in Table 5.13. Appendix IV provides a detailed record of TG/DTA of one sample.

Table 5.13: $\text{Ca}(\text{OH})_2$ content of hydrated cements from TG analysis

Sample	loss due to decomposition of $\text{Ca}(\text{OH})_2$		mass of $\text{Ca}(\text{OH})_2$	calculated % of $\text{Ca}(\text{OH})_2$
	%	mass, g		
Rh	5.90	0.35	1.45	24.58
5S	2.89	0.56	2.33	12.05
5Sh	2.66	0.45	1.89	11.07
5L	1.07	0.56	2.33	12.89
5P	2.98	0.52	2.15	12.43
5P5L	2.63	0.52	2.18	11.00
2.5P2.5Sh5S	1.20	0.19	0.80	5.02
5P5L5S	1.52	0.30	1.26	6.31
2.5P2.5L2.5Sh5S	1.55	0.30	1.23	6.46

5.6 Mechanical and engineering properties

The various mix designs employed in the moulding of mortar and concrete specimens for the compressive and flexural strength tests are given in Table 5.14. The mixes were used to achieve compressive strengths of between 32.5MPa and 42.5 MPa for the mortar cubes, and 20 MPa for the concrete specimen at 28 days.

Table 5.14: Mortar and concrete mix design details by ratio and mass of materials

Sample	Mix proportion by mass			W/C	Mass (g)			
	Cement blend	Sand	Crushed aggregate		Cement blend	Sand	Crushed aggregate	Water
Mortar cubes	1	3	-	0.5	300	900	-	150
Concrete cubes	1	2	4	0.6	1500	3000	6000	900
	1	2	4	0.55	1500	3000	6000	825
Concrete prisms	1	2	4	0.6	250	500	1000	150
Concrete Beam	1	2	4	0.6	300	600	1200	180

The results of the mortar compressive strength tests of the reference and blended cements with different admixture contents up to 365 days are given in Tables 5.15 and 5.16. The percentage of the strength of blended cements relative to that of reference cement at 28 and 365 days are presented in Tables 5.17-5.18. The compressive strengths of the blended concretes up to 365 days, analysis of their percentage to the reference at 28 days and 365 days and the increase of strength from 28 to 365 days using $w/c = 0.6$ are given in Table 5.19. Comparative results of selected concrete specimens using $w/c = 0.55$ and 0.6 are presented in Table 5.20. The results of the flexural tensile strength tests are presented in Table 5.21.

Table 5.15: Compressive strengths of reference and blended cement

Type	Sample	Clay					Compressive strength, MPa				
		Cement	Steel slag	Pozzolana	Shells	Limestone	2days	7days	28days	90 days	365 days
		Content, %									
	Reference	100	–	–	–	–	22.6	31.7	43.2	43.5	43.8
Binary	5S	95	5	–	–	–	19.4	25.1	42.3	42.4	42.5
	5P	95	–	5	–	–	20.7	26.2	42.8	42.9	43.5
	5Sh	95	–	–	5	–	21.6	26.8	43.0	43.1	43.5
	5L	95	–	–	–	5	22.9	29.2	42.1	42.3	43.0
Ternary (5%x5%y)	5S5Sh	90	5	–	5	–	16.5	24.3	41.0	41.4	42.0
	5S5P	90	5	5	–	–	17.1	25.1	41.8	42.1	43.1
	5S5L	90	5	–	–	5	19.5	23.5	40.9	42.2	43.0
	5P5Sh	90	–	5	5	–	16.6	24.1	40.4	42.0	42.5
	5P5L	90	–	5	–	5	21.4	24.1	41.1	41.7	42.7
	5Sh5L	90	–	–	5	5	18.7	22.4	40.1	41.2	41.2
(10%x5%y)	10S5Sh	85	10	–	5	–	16.8	24.2	40.0	40.3	41.3
	5S10Sh	85	5	–	10	–	14.6	20.3	40.5	40.8	40.5
	10S5P	85	10	5	–	–	17.0	23.9	39.5	40.0	40.2
	5S10P	85	5	10	–	–	16.7	24.5	39.7	40.2	41.1
	10S5L	85	10	–	–	5	15.2	24.0	39.7	40.6	42.0
	5S10L	85	5	–	–	10	14.2	20.8	39.0	39.0	40.5
	10P5Sh	85	–	10	5	–	14.9	23.3	40.0	40.3	42.1
	5P10Sh	85	–	5	10	–	15.0	19.5	39.7	40.2	41.1
	10P5L	85	–	10	–	5	14.0	20.0	39.7	41.1	42.0
	5P10L	85	–	5	–	10	14.6	20.2	39.8	40.5	41.3
	5Sh10L	85	–	–	5	10	14.5	19.7	38.4	39.2	40.6
	10Sh5L	85	–	–	10	5	14.7	20.1	38.6	39.1	41.3

Table 5.16: Compressive strengths of reference and blended cement mortars

Type	Sample	Cement	Steel slag	Pozzolana	Shells	Limestone	Compressive strength, MPa				
		Content, %					days				
							2	7	28	90	365
Ternary (10%x10%y)	10S10P	80	10	10	–	–	14.2	19.6	39.4	40.2	41.7
	10S10L	80	10	–	–	10	13.9	18.3	37.5	40.1	40.5
	10S10Sh	80	10	–	10	–	13.4	16.9	39.0	40.4	42.0
	10P10Sh	80	–	10	10	–	13.6	23.7	39.1	40.5	42.3
	10P10L	80	–	10	–	10	13.9	22.4	38.0	40.0	41.6
	10Sh10L	80	–	–	10	10	13.9	20.6	38.0	40.6	42.0
Quaternary (5%x5%y5%z) (2.5%x2.5%y2.5%z)	5S5P5Sh	85	5	5	5	–	14.0	21.1	39.1	40.3	40.6
	5S5P5L	85	5	5	–	5	13.7	20.6	39.6	40.3	42.7
	5S5Sh5L	85	5	–	5	5	13.4	20.2	37.8	39.5	41.1
	5P5Sh5L	85	–	5	5	5	14.8	20.0	39.7	41.7	42.5
	2.5S2.5P2.5Sh	92.5	2.5	2.5	2.5	–	18.7	24.1	42.3	42.4	43.5
	2.5S2.5P2.5L	92.5	2.5	2.5	–	2.5	18.6	23.8	42.1	43.6	44.1
	2.5S2.5Sh2.5L	92.5	2.5	–	2.5	2.5	18.0	23.6	41.7	42.0	43.8
	2.5P2.5Sh2.5L	92.5	–	2.5	2.5	2.5	17.9	23.7	42.0	42.3	43.0
Quinternary	2.5S2.5P2.5Sh2.5L	90	2.5	2.5	2.5	2.5	17.1	23.8	41.7	42.1	43.2
	5S5P5Sh5L	80	5	5	5	5	15.1	22.5	38.7	38.1	41.7

Table 5.17: Analysis of strength of blended cement to reference cement mortars

Type	Sample	Compressive strength, MPa					% of reference strength at 28 days	% of reference strength at 365 days
		2days	7 days	28days	90 days	365 days		
	Rc	22.6	31.7	43.2	43.5	43.8	100.0	100.0
Binary	5S	19.4	25.1	42.3	42.4	42.5	97.9	97.0
	5P	20.7	26.2	42.8	42.9	43.5	99.1	99.3
	5Sh	21.6	26.8	43.0	43.1	43.5	99.5	99.3
	5L	22.9	29.2	42.1	42.3	43.0	97.5	98.2
Ternary (5%x5%y)	5S5Sh	16.5	24.3	41.0	41.4	42.0	94.9	95.9
	5S5P	17.1	25.1	41.8	42.1	43.1	96.8	98.4
	5S5L	19.5	23.5	40.9	42.2	43.0	94.7	98.2
	5P5Sh	16.6	24.1	40.4	42.0	42.5	93.5	97.0
	5P5L	21.4	24.1	41.1	41.7	42.7	95.1	97.5
	5Sh5L	18.7	22.4	40.1	41.2	41.2	92.8	94.1
(10%x5%y)	10S5Sh	16.8	24.2	40.0	40.3	41.3	92.6	94.3
	5S10Sh	14.6	20.3	40.5	40.8	40.5	93.8	92.5
	10S5P	17.0	23.9	39.5	40.0	40.2	91.4	91.8
	5S10P	16.7	24.5	39.7	40.2	41.1	91.9	93.8
	10S5L	15.2	24.0	39.7	40.6	42.0	91.9	95.9
	5S10L	14.2	20.8	39.0	39.0	40.5	90.3	92.5
	10P5Sh	14.9	23.3	40.0	40.3	42.1	92.6	96.1
	5P10Sh	15.0	19.5	39.7	40.2	41.1	91.9	93.8
	10P5L	14.0	20.0	39.7	41.1	42.0	91.9	95.9
	5P10L	14.6	20.2	39.8	40.5	41.3	92.1	94.3
	5Sh10L	14.5	19.7	38.4	39.2	40.6	88.9	92.7
	10Sh5L	14.7	20.1	38.6	39.1	41.3	89.4	94.3

Table 5.18: Analysis of strength of blended cement to reference cement mortars

		Compressive strength, MPa					% of control Strength at 28 days	% of control Strength at 365 days
		Days						
Type	Sample	2	7	28	90	365		
Ternary (10%x10%y)	10S10P	14.2	19.6	39.4	40.2	41.7	91.2	95.2
	10S10L	13.9	18.3	37.5	40.1	40.5	86.8	92.5
	10S10Sh	13.4	16.9	39.0	40.4	42.0	90.3	95.9
	10P10Sh	13.6	23.7	39.1	40.5	42.3	90.5	96.6
	10P10L	13.9	22.4	38.0	40.0	41.6	88.0	95.0
	10Sh10L	13.9	20.6	38.0	40.6	42.0	88.0	95.9
Quaternary (5%x5%y5%z)	5S5P5Sh	14.0	21.1	39.1	40.3	40.6	90.5	92.7
	5S5P5L	13.7	20.6	39.6	40.3	42.7	91.7	97.5
	5S5Sh5L	13.4	20.2	37.8	39.5	41.1	87.5	93.8
	5P5Sh5L	14.8	20.0	39.7	41.7	42.5	91.9	97.0
(2.5%x2.5%y2.5%z)	2.5S2.5P2.5Sh	18.7	24.1	42.3	42.4	43.5	97.9	99.3
	2.5S2.5P2.5L	18.6	23.8	42.1	43.6	44.1	97.5	100.7
	2.5S2.5Sh2.5L	18.0	23.6	41.7	42.0	43.8	96.5	100.0
	2.5p2.5Sh2.5L	17.9	23.7	42.0	42.3	43.0	97.2	98.2
Quinternary	2.5S2.5P2.5Sh2.5L	17.1	23.8	41.7	42.1	43.2	96.5	98.6
	5S5P5Sh5L	15.1	22.5	38.7	38.1	41.7	89.6	95.2

Table 5.19: Analysis of strength of blended cement to reference cement concretes

Material	water/ cement	Slump, Mm	Compressive strength, MPa					% of control strength at 28 days	% of control strength at 365 days	% increase of strength from 28 to 365 days
			Days							
			2	7	28	90	365			
Rh	0.6	72	13.3	17.3	22.5	23.9	31.1	100.0	100.0	38.2
5S	0.6	74	12.9	16.0	21.0	21.6	28.7	93.3	92.3	36.7
5Sh	0.6	78	12.8	15.3	21.8	22.7	29.0	96.9	93.2	33.0
5L	0.6	73	13.4	15.7	21.6	22.5	27.7	96.0	89.1	28.2
5P	0.6	65	12.4	15.8	21.7	21.8	25.0	96.4	80.4	15.2
5S5Sh	0.6	73	11.1	15.0	19.5	22.3	28.4	86.7	91.3	45.6
5L5S	0.6	70	11.4	14.7	19.1	22.4	30.1	84.9	96.8	57.6
5L5Sh	0.6	78	10.8	14.1	18.4	22.0	27.2	81.8	87.5	47.8
5P5S	0.6	65	10.9	15.0	20.0	22.9	26.9	88.9	86.5	34.5
5P5Sh	0.6	68	10.9	14.8	19.3	22.7	29.0	85.8	93.2	50.3
5P5L	0.6	70	10.8	14.4	18.6	21.5	27.3	82.7	87.8	46.8
5L 5Sh 5S	0.6	76	10.3	15.8	17.2	21.1	25.4	76.4	81.7	47.7
5P 5Sh5S	0.6	70	10.6	14.2	19.1	21.7	27.8	84.9	89.4	45.5
5P5L5S	0.6	71	10.4	14.3	18.1	20.1	26.5	80.4	85.2	31.8
5P5L5Sh	0.6	66	10.2	13.7	18.4	21.0	26.0	81.8	83.6	41.3
2.5L 2.5Sh 2.5S	0.6	72	11.7	12.5	20.6	21.3	29.6	91.6	95.2	43.7
2.5P 2.5Sh2.5S	0.6	70	11.7	12.8	20.8	21.9	26.6	92.4	85.5	27.9
2.5P2.5L2.5S	0.6	68	12.2	12.2	21.4	22.0	27.7	95.1	89.1	29.4
2.5P2.5L 2.5Sh	0.6	70	11.7	12.2	21.0	20.8	28.0	93.3	90.0	33.3
2.5P2.5L2.5Sh2.5S	0.6	71	10.9	12.1	19.8	21.8	28.0	88.0	90.0	41.4
5P5L 5Sh5S	0.6	78	10.5	10.7	17.2	19.5	24.6	76.4	79.1	43.0

Table 5.20: Comparative compressive strengths of 1:2:4 cement concrete using different water - cement ratios

Sample	Slump, mm		28-day Compressive strength	
	w/c=0.55	w/c=0.6	w/c=0.55	w/c=0.6
Rh	75	72	25.47	22.5
5S	76	74	24.1	21.0
5Sh	74	78	24.0	21.8
5L	76	73	24.3	21.6
5P	78	65	24.6	21.7
5L5S	77	70	24.3	19.1
5P5S	74	65	22.5	20.0
5P5L	78	70	22.9	18.6
5Sh5L	79	78	22.8	18.4
5S5Sh	74	73	24.0	19.5
5P5Sh	75	68	22.3	19.3
5P5L5S	72	71	19.4	18.1
5L5Sh5S	77	76	20.4	17.2
5P5Sh5S	73	70	19.7	19.1
5P5L5Sh	73	66	19.1	18.4
2.5P2.5L2.5S	73	68	21.7	21.4
2.5L2.5Sh2.5S	75	72	22.3	20.6
2.5P2.5Sh2.5S	70	70	21.4	20.8
2.5P2.5L2.5Sh	70	70	22.1	21.0
2.5L2.5S2.5Sh	74	71	21.2	19.8
5P5L5S5Sh	72	78	19.1	17.2

Table 5.21: Tensile strengths of 1:2:4 cement concrete using different water to cement ratios

Sample	28 – day Strength, MPa			% of Tensile to compressive strength	
	Compressive	Tensile			
		w/c = 0.60	w/c = 0.55	w/c = 0.60	w/c = 0.55
Rh	43.2	4.5	6.0	10.42	13.89
5S	42.3	4.5	5.4	10.64	12.77
5Sh	43.0	4.5	5.2	10.47	12.09
5L	42.1	4.5	5.4	10.69	12.83
5P	42.8	4.5	5.4	10.51	12.62
5L5S	40.9	3.7	4.6	9.05	11.25
5P5S	41.8	3.6	4.4	8.61	10.53
5P5L	41.1	4.5	5.0	10.95	12.17
5Sh5L	40.1	3.6	4.8	8.98	11.97
5S5Sh	41.0	3.6	4.8	8.78	11.71
5P5Sh	40.4	4.1	5.2	10.15	12.87
5P5L5S	42.7	4.0	4.4	9.37	10.30
5L5Sh5S	41.1	3.6	4.3	8.76	10.46
5P5Sh5S	40.6	3.8	5.3	9.36	13.05
5P5L5Sh	42.5	3.6	5.4	8.47	12.71
2.5L2.5Sh2.5S	43.8	4.5	5.2	10.27	11.87
2.5P2.5Sh2.5S	43.5	4.0	4.8	9.20	11.03
2.5P2.5L2.5S	44.1	4.3	4.8	9.75	10.88
2.5P2.5L2.5Sh	43.0	4.5	5.0	10.47	11.63
2.5L2.5S2.5Sh	43.2	4.8	6.2	11.11	14.35
5P5L5S5Sh	41.7	3.6	4.8	8.63	11.51

5.7 Durability Test

5.7.1 Sulphate and Chloride resistance

Table 5.22 presents the compressive strengths of the mortar cubes in both solutions at 28 days. The decrease in strength compared to that immersed in water as well as their water absorption values in the solutions are also provided. The compressive strengths of the various blended cement mortars in sodium sulphate solution and seawater and the reduction in strength at from 28 to 365 days are presented in Tables 5.23 and 5.24 respectively.

Table 5.22: Compressive strength of mortar cubes immersed in Na₂SO₄ solution and seawater (NaCl) at 28 days

Sample	Compressive strength, MPa			% decrease in strength		Water Absorption, %	
	Water	Seawater	Na ₂ SO ₄	Seawater	Na ₂ SO ₄	Na ₂ SO ₄	Sea water
Rh	43.2	32.2	33.1	25.5	23.38	1.44	1.15
5Sh	43.0	27.3	28.2	36.5	34.42	1.62	1.37
5P	42.8	29.4	35.1	31.3	17.99	1.33	1.22
5L	42.1	28.4	33.5	32.5	20.43	1.38	1.09
5S	42.3	35.6	24.5	15.8	42.08	1.32	1.02
5P5Sh	41.1	29.2	38.8	29.0	5.60	1.26	1.14
5L5Sh	40.1	29.4	39.1	26.7	27.4	1.28	1.10
5L5S	40.9	30.2	35.7	26.2	12.71	1.17	1.11
5P5Sh	40.4	31.2	35.6	22.8	11.88	1.17	1.10
5Sh5S	41.0	32.0	32.1	22.0	21.71	1.17	1.19
5P5S	41.8	33.4	34.1	20.1	18.42	1.28	1.11
5P5S5Sh	39.1	29.8	30.9	23.8	20.97	1.28	1.14
5P5L5Sh	39.7	30.6	38.8	22.9	2.27	1.28	1.11
5P5L5S	39.6	30.6	30.6	22.7	22.73	1.17	1.40
5L5Sh5S	37.8	34.7	33.1	8.2	12.43	1.13	1.07
2.2P2.5L2.5Sh2.5s	41.7	33.7	39.1	19.2	6.24	1.04	1.23
5P5L5Sh5S	38.7	29.0	35.6	25.1	8.01	1.06	1.19

Table 5.23: Compressive strength of blended cement mortar cubes immersed in seawater (NaCl)

Sample	Compressive strength, MPa			% reduction	Water absorption, %			% change
	Days			of strength	Days			
	28	90	365	28-365days	28	90	365	
Rh	32.2	32.6	27.4	14.91	1.15	1.24	1.28	10.16
5S	35.6	27.6	27.6	22.47	1.02	1.12	1.25	18.40
5Sh	27.3	26.0	25.5	6.59	1.37	1.23	1.18	-16.10
5P	29.4	27.8	25.8	12.24	1.22	1.30	1.25	2.40
5L	28.4	26.4	24.9	12.32	1.09	1.16	1.33	18.05
5Sh5S	32.0	25.8	26.7	16.56	1.19	1.24	1.33	10.53
5L5S	30.2	27.7	28.0	7.28	1.11	1.20	1.09	-1.83
5P5S	33.4	29.0	27.7	17.07	1.11	1.08	1.29	13.95
5P5Sh	31.2	28.3	27.1	13.14	1.10	1.13	1.31	16.03
5L5Sh	39.4	28.8	25.6	35.03	1.10	1.25	1.23	10.57
5P5L	29.2	26.7	28.5	2.40	1.14	1.30	1.31	12.98
5L5Sh5S	34.7	28.8	26.8	22.77	1.11	1.08	1.20	7.50
5P5Sh5S	29.8	26.8	23.8	20.13	1.40	1.32	1.33	-5.26
5P5L5S	30.6	28.7	28.0	8.50	1.23	1.29	1.27	3.15
5P5L5Sh	30.8	29.0	24.7	19.81	1.23	1.32	1.36	9.56
5P5L5Sh5S	29.0	29.0	23.8	17.93	1.14	1.03	1.17	2.56
2.5P2.5L2.5Sh2.5S	33.7	27.0	28.4	15.73	1.07	1.15	1.29	17.05

Table 5.24: Compressive strength of blended cement mortar cubes immersed in Na₂SO₄ solution

Sample	Compressive strength, MPa			% reduction from 28- 365 days	Solution absorption, %			% Change
	Days				Days			
	28	90	365		28	90	365	
Rh	33.1	27.2	25.2	23.87	1.44	1.41	1.47	2.04
5S	24.5	23.1	22.6	7.76	1.32	1.38	1.36	2.94
5Sh	28.2	24.6	25.3	10.28	1.62	1.37	1.42	-14.08
5P	35.1	27.1	26.8	23.65	1.33	1.38	1.45	8.28
5L	33.5	25.3	24.1	28.06	1.38	1.34	1.43	3.50
5Sh5S	32.1	28.5	25.1	21.81	1.17	1.30	1.41	17.02
5L5S	35.7	27.0	26.2	26.61	1.17	1.30	1.34	12.69
5P5S	34.1	27.3	25.6	24.92	1.28	1.30	1.37	6.57
5P5Sh	35.6	28.1	23.7	33.43	1.17	1.28	1.39	15.83
5L5Sh	39.1	27.5	23.9	38.87	1.28	1.35	1.35	5.19
5P5L	38.8	26.6	24.5	36.86	1.26	1.35	1.41	10.64
5L5Sh5S	33.1	23.5	26.2	20.85	1.13	1.19	1.26	10.32
5P5Sh5S	30.9	25.6	23.3	24.60	1.28	1.31	1.28	0.00
5P5L5S	30.6	27.2	24.1	21.24	1.17	1.25	1.31	10.69
5P5L5Sh	38.8	26.5	25.1	35.31	1.28	1.34	1.35	5.19
5P5L5Sh5S	35.6	25.9	22.3	37.36	1.06	1.26	1.32	19.70
2.5P2.5L2.5Sh2.5S	39.1	28.4	27.1	30.69	1.04	1.23	1.41	26.24

CHAPTER SIX

DISCUSSIONS

6.0 Introduction

This chapter analyses all the test results obtained and presented in Chapter Five. It also discusses the significance of the results with respect to the suitability of the blended cements for concrete and general construction using the standard specifications of British, European, Ghanaian and Indian Standards. The results are compared to that of the reference cement and similar works of other researchers. Finally, the effect on the hydration products by the admixtures and the positive resistance of the blended cements to the acidic waters are discussed.

6.1 Physical properties

6.1.1 The particle size distribution and sieve analysis of aggregates and admixtures

The particle size distribution curves of the sieved sand (Fig. 5.2) show that the sand was mostly coarse, 95% of it within the 0.5mm and 2mm range. In addition, it did not contain any fines ($< 75\mu\text{m}$). The silt content of sand was however 4.5%, greater than the required content of 2%.

Between 75% and 98% of the admixtures were below $50\mu\text{m}$ size (Fig. 5.3), except slag that gave a low figure of 30%. This gives an indication that blended cements may produce appreciable strengths since fineness plays an important role in strength development. A detailed sieve analysis of the aggregates, given in Table 5.2, shows that the fine and coarse aggregates satisfy BS 882 (1992).

The grading of the aggregates, complied with the BS 882:1990 for a 20-5mm graded coarse aggregates and the fine aggregates close to the medium sand. The mineral grains of the crushed aggregates were large enough to be seen exhibited and possessed colour that range from white to grey. The granitic aggregates are thus of good quality and therefore suitable for concrete works as per the standard specifications.

6.1.2 Specific gravity, soundness and fineness

The specific gravity of the admixtures ranged between 2.59 and 2.85 (Table 5.1), and that of the blended cements between 2.7 and 3.1, lower than that of reference value of 3.16 (Table 5.4). This is so since all the admixtures were less dense than the reference cement (Table 5.1). The specific gravity of the blended cements gave indication that they would provide dense concretes. It is evident from Table 5.3 that Blaine surface area of the cements was increased by addition of admixtures for the same residue on the 45- μ m sieve. On the average, surface area increased approximately by at least 70m²/kg. Pozzolana blended cements gave the highest surface area with 5%Pozzolana5%shell cement of 525 m²/kg. The high Blaine values obtained give indication of high early strengths and comparable strengths of Class 32.5N and 42.5N Portland cement. The soundness tests on the blended cements showed that they expanded less than the reference cement (Table 5.4).

6.1.3 Water Permeability

Permeability is an important property related to the durability of cementitious materials. It is defined as that property which characterizes the ease with which a fluid passes into and through the body of the concrete under a pressure gradient (Basheer, 2001). Concrete

with low permeability exhibits good resistance to sulphate attack, chloride attack and alkali-silica reaction, since water carrying aggressive ions are difficult to penetrate into concrete pore structure (Bakker, 1983; Feldman, 1986).

From Table 5.5, the results of the permeability tests showed clearly that addition of the admixtures, except slag, reduced the porosity of the cement by at least 4% and as much as 20%. This agrees with the assertion that admixtures fill the pores of cement products making it less porous (Hawkins *et al*, 2003; Bonavettiet *al*, 2001; Péraet *al*, 1999; Soroka and Setter, 1977). Pozzolana cement gave the least permeability of 3.39×10^{-4} as compared to 4.42×10^{-4} of reference cement. Slag cement was more porous than the reference and this could be attributed to the relatively larger particle size as compared to the other admixtures (Fig. 5.3).

6.1.4 Water demand and setting times

The water demand and setting times of the reference and blended cements, as presented in Table 5.4, showed that the water demand of the blended cements ranged from 24.5% to 34.2% and that it increased as the percentage replacements of cement are increased. However, replacing cement with up to 10% of admixtures did not change the demand significantly except 5%pozzolana5%limestone cement. Cement pastes containing admixtures over 10% recorded values above 30% and this is due to the fact that increase in the amount of admixtures involves a decrease in the amount of cement (dilution effect) and consequently, an increase in the effective water cement ratio resulting in higher water demand (Adesanyaand Raheem,2009; Alamet *al*, 2006; Mehta, 1981). The addition of limestone/shell (CaCO_3) and clay pozzolana increased the plasticity of the mix, which needed more water for workability. In

addition, CaCO_3 and clay pozzolana increase the effective reactive surface area, increases capacity to absorb water, and the reaction of CaCO_3 with C_3A to form carboaluminate hydrates leads to the higher need of water than calcium silicate hydrates (Heikalet *al*, 2000, Soroka, and Setter1977).

The initial setting times (<95min) of 5%x and 5%x5%y blended cements were lower than reference cement. This is so because there is always an interaction between tricalcium silicate (C_3S) and the admixtures, with the latter accelerating the hydration of C_3S and modifying the Ca/Si ratio of calcium silicate hydrates. Also, admixtures provide additional surface area which accelerates hydration (Heikalet *al*, 2003, Sorokaand Setter, 1977). Increasing the amount of admixtures prolongs the initial setting times of the blended cements and thus is attributed to the decrease of C_3A content of cement. Nevertheless, the initial and final setting times obtained for all cement blends were more than 75 minutes and less than 10 hours respectively for the final as stipulated by EN 197-1 (2000) and GS:22 (2004). The slag containing cements normally demanded less water than the rest which can be attributed to the delayed hydration of the slag, due to its mineralogical composition and the relatively high MgO andMnO content (Table 3.2) as stated byKourouniset *al* (2007).

6.2 Chemical properties of cement samples

The chemical compositions of the mineral admixtures are very essential in determining their suitability as appropriate minerals for blending cement. Studies have shown that chemical activity of admixtures in cement is dependent essentially on their lime, silica and alumina contents (Lea, 1970). The XRF determination, converted to its oxide composition, are provided in Tables 5.6 – 5.8. The CaO , SiO_2 , Fe_2O_3 and

Al_2O_3 determined are mainly constituents of hydrated calcium silicate (C_3S and C_2S), calcium aluminates (C_3A) and calcium aluminoferrite (C_4AF), the main essential compounds needed for cement hydration for strength development. The CaO - and silica-containing phases of cement are very important because the strength development and stability of cement products depend mostly on the two compounds as described in Section 2.1.1 in Chapter 2.3 and 2.4. Compared with reference cement, the lime contents of the blended cements were reduced, except 5% shell cement because of its relatively higher CaO content. However, the silica contents of the 5%slag and 5%pozzolana cement blends were higher than the reference cement as a result of the higher silica content of Pozzolana and slag. This gives an indication that the binary cements would produce satisfactory results in terms of strength as explained in Chapter 2..

The iron oxide content of the binary cements ranged between 3.1% and 5.25% as compared to 4.36% of reference cement because of the high silica content of the admixtures, particularly pozzolana and steel slag. (Table 5.6). However, the alumina content was very low (3.2%) for 5%shell cement because of shell's low alumina content and quite high (5.5% and 6.1%) for 5%pozzolana and 5%limestone cements. Alumina makes little direct contribution to the strength of Portland cement but accelerates the hydration of cement. Iron oxide in cement has no effect on cement but acts as flux to aid cement and gives the grey colour of cement (Lea, 1970). All the binary compounds contained less than 3% MgO .

The alkali content of the blended cements was quite significant, between 4.35 and 8.6%. Effects of alkalis in strength development are not fully understood but studies

have shown that higher levels of alkalis lower strength gain of cement beyond 28 days. However, the total absence of alkalis results in abnormally low early strength [Lea, 1970; Neville, 2000]. The sulphate and chloride contents of the binary cements were lower than the standard limit of 3.5% and 0.10% respectively (EN 197-1). This is quite positive because excess SO_3 leads to formation of sulphonates that cause expansion in cement concretes which are detrimental to cement strength and durability (Odler and Gasser, M, 1988). The other minor constituents like TiO_2 , MnO_2 and P_2O_3 were less than 0.5% and have no effect on strength and properties of cement products.

The CaO contents of the 5%*x*5%*y* ternary cement blends were above 52% except 5%pozzolana5%slag cement which gave a value of 50.41% (Table 5.6). Even though the CaO values are lower than the reference cement (Table 3.2) by at least 2.1% the chemical compositions of the 5%*x*5%*y* cement blends (Table 5.6) meet the minimum percentage requirement needed to give expected reactivity during hydration to produce the strengths and soundness expected to meet minimum values specified by EN 197-1(2000). The silicon dioxide contents of between of 18.5% and 24.5% also give a positive indication of their reactivity during hydration. The MgO content was less than 5% and that of TiO_2 , MnO_2 and P_2O_3 were below 0.5%. The SO_3 and chloride contents were lower than the standard limit of 3.5% and 0.1% respectively (EN 197-1)

Tables 5.7 presents the chemical compositions of 10%*x*5%*y* ternary and 5%*x*5%*y*5%*z* quaternary blended cements with a cement replacement of 15% whilst that of 10%*x*10%*y* ternary, 2.5%*x*2.5%*y*2.5%*z*2.5%*p* and 5%*x*5%*y*5%*z*5%*p*

quinternary blended cements are shown in Table 5.8. The lime contents of these cements ranged from 43.67% to 54.78%. Obviously, samples with less than 50% CaO will record relatively lower strength. The silica content was between 13.95% and 25.61%. The iron oxide and alumina contents of these blends ranged from 2.39% to 6.44% and 1.86 to 5.95% respectively, with slag blended samples giving appreciable values.

6.3 Mineralogy of hydrated blended cements

6.3.1 Infrared Spectrometry

The IR spectra of hydrated 5% binary and 5% $\times$ 5% blended cements at 7 days and 28 days are shown in Figs. 5.4 -5.6, and also summarized in Tables 5.9 - 5.10. In the high zone the peak at 3645cm^{-1} is assigned to the O-H stretching of $\text{Ca}(\text{OH})_2$ formed whilst the peaks at 970 cm^{-1} is attributed to calcium silicate hydrate (C-S-H). The broad band at $3600\text{-}3000\text{ cm}^{-1}$ is due to symmetric and asymmetric stretching (ν_1 and ν_3) of the O-H vibration of the water molecule which is more intense in 28 days hydration spectrum. Deformation of water band at 1645 cm^{-1} is present in both spectra. The CO_3^{2-} bands (ν_3, ν_2) at 1480 cm^{-1} and 875 cm^{-1} are diminished for both spectra of 5% shell and 5% limestone cement blends compared to other admixtures indicating the significant influence of CaCO_3 in the hydration process. Also, some SiO_4 and CO_3 bands were shifted after 7 days due to admixture reactions. The 1120 cm^{-1} and at $\nu_3\text{SO}_4^{2-} 1100\text{ cm}^{-1}$ bands are attributed to ettringite (*Aft*) and monosulphonate (*Afm*) phases respectively and were present in both spectra. The main characteristic of the hydrated samples at 970 cm^{-1} accounts for the polymerization of the units SiO_4^{4-} present in C_3S and C_2S . The peaks at $450 - 460\text{ cm}^{-1}$ signifies the presence of calcium aluminate and aluminosilicate hydrates which

gave the same intensity for both spectra (Trezza, 2007; Pera et al, 1999). The ettringite and monosulphonate of CaCO_3 -based admixtures (that is, limestone and shell cement) bands were almost flat or disappeared compared to others, indicating increased reactivity between CO_3^{2-} and SiO_4^{4-} ions. Also, their near absence will improve the durability of the cement against sulphates and chlorides. At 28 days, both bands are considerably reduced in the case of slag and pozzolana. The $\nu_2, \nu_4 \text{SiO}_4^{4-}$ bands at 462 cm^{-1} and 518 cm^{-1} are present in both spectra but more intense in 28 days hydration spectrum. The main characteristic of the hydrated samples is the absence of $\nu_4 \text{SiO}_4^{4-}$ band at 640 cm^{-1} in 7 days hydration spectrum.

The CO_3 and SiO_4 ion bands decreased as the hydration days increased for all the samples. The ettringite bands increased as the hydration days increased whilst SO_4 bands decreased and this could be due to replacement of SO_4 ions in ettringite by CO_3 ions. On the contrary, 5%pozzolana5%slag cement and 5%shell5%limestone cement spectra have their $\nu_3 \text{SO}_4$ bands and $\nu_3 \text{SiO}_4$ bands increasing as the hydration days increased therefore their bands in the 7 days hydrated samples have weak intensities unlike their 28 days spectra which have strong intensities. It could be deduced that the chemical reactions that led to their formation was slow as compared to that of the control and the other spectra which seem to be rapid.

Ettringite band at 1100 cm^{-1} is present in all the samples. The band at 3450 cm^{-1} in the samples is the symmetric and asymmetric stretching (ν_1 and ν_3) of O-H of the water molecules, although, there are some slight differences in the intensities of the bands; they all have the same wave number. The $\nu_3 \text{SO}_4$ bands are present at 1000 cm^{-1} although the band is indistinguishable from that of $\nu_3 \text{SiO}_4$.

6.3.2 X-Ray diffraction analysis

The X-Ray diffraction graphs show ettringite formation and all clinker minerals, namely alite (C_3S), belite (C_2S), calcium aluminate (C_3A), and ferrite (C_4AF) as well as portlandite ($Ca(OH)_2$). From Table 5.11 the portlandite [$Ca(OH)_2$] content is considerably reduced from 36.9% of reference cement to between 9.1% and 13.4% as a result of admixture reactions. Reduction of $Ca(OH)_2$ in cement product reduces the susceptibility of the blended cement to acidic attack. However, the formation of ettringite was enhanced considerably from 9.1% in reference cement to 15.5% in 5% shell cement, 33.2% in 5% pozzolana cement and 35.3% in 5% limestone cement and 21.7% in 5% pozzolana 5% slag cement. However, the percentage was reduced to 6.5% in 5% pozzolana 5% limestone cement. The increase in ettringite will lead to reduction in its tendency to transform to the calcium aluminate monosulphate that affects the stability of cement products and makes it more susceptible to sulphate attack.

6.3.3 Microstructure and EDX analysis of cement samples

The micrographs (Figs. 5.13 – 5.21) from the SEM graphs indicated clearly that the pores of the blended cement were reduced as a result of addition of admixtures, except 5% limestone cement. The elemental composition (Table 5.12) from the Electron Dispersive X-ray (EDX) analysis showed that the Ca element reduced from 32.6% to between 25% and 31.7% in the blended cements. However, the mass percentage of oxygen (O) and silicon (Si), increased by at least 6.5% and 5% (except 5% shell 5% slag cement) respectively in the blended cements. Since $Ca(OH)_2$ had been observed to have reduced in the blended compared to the reference cement

from the Infrared (IR) and XRD analysis, it can be concluded that the increase in these elements will lead to increase amounts of calcium silicate compounds (C_3S and C_2S) which are essential to mechanical properties of cement. That is actually confirmed by the higher peaks of C_3S of the blended cements from the XRD graphs of Figs. 5.7 and 5.8, which give an indication of high early compressive strength. Also, reduction in $Ca(OH)_2$ is an additional advantage as it is a potential source of acidic attack which weakens and deteriorates concrete.

6.3.4 Thermoanalysis of raw samples and hydrated blended cements

Chemically, the steel slag contains iron oxide, silica, lime, aluminium oxide and MgO (Table 4.4). Heating of lime in the presence of silica to $1000^{\circ}C$ yields calcium silicate products. Formation of the compound $CaO.SiO_2$ started at an endothermic peak of $607^{\circ}C$ (check Appendix IV). The endothermic peak at $651^{\circ}C$ was the conversion of the product formed to the metastable $\beta-CaO.SiO_2$. The formation of the $\alpha-CaO.SiO_2$ phase began at $684.9^{\circ}C$ which was due to the conversion of the metastable state. Crystallization of the final product of stable hydrated calcium silicate occurred by an endothermic reaction at $977.7^{\circ}C$. Total loss of mass was about 1.8% (Fig. 5.22).

The main chemical component of limestone is $CaCO_3$. The endothermic peaks between $600^{\circ}C$ and $690^{\circ}C$ were due to decomposition of $CaCO_3$ leading to the evolution of carbon dioxide. The DTA endothermic peak at $733^{\circ}C$ signifies the phase change (decomposition) of calcite to CaO (Appendix IV). There was a total mass change of about 34%. This is less than the expected 44% because of presence of impurities like sand(SiO_2) in the limestone used (Table 4.) The thermal effect and

phases changes for clam shells are similar to that of limestone since both contain mainly CaCO_3 . Evolution of CO_2 occurred between 666°C and 754°C whilst the phase change occurred at 740°C . The total loss of mass for the shells was about 35%.

When the clay sample was heated, a number of reactions took place which caused a series of mineralogical and crystallographic changes. An endothermic reaction, which resulted in the removal of nearly all the physically bound water occurred from 30°C to 176°C . The endothermic peaks at 435°C showed the expulsion of structural water principally from the crystal lattice of kaolinite with a mass loss of about 0.15%. As the temperature increased, dehydroxylation of the clay and formation of quasi-amorphous material, metakaolin, which is reactive with lime occurred around 635°C . Endothermic reactions which result from the removal of crystal lattice water are the most critical ones from the pozzolanic activity point of view. Each clay has an optimum calcination temperature which produces high pozzolanic activity. This temperature is just above the completion of the dehydroxylation peak and below the onset of the re-crystallization peak.

Figure 5.18 presents the thermogram of reference cement sample. The endothermic peak between 26°C and 142°C represented the evaporation of water molecules and dehydration of calcium silicate hydrate (C-S-H), formation of ettringite, decomposition of gypsum (Lea, 1970). Dehydroxylation of $\text{Ca}(\text{OH})_2$ (portlandite) occurred from 404°C to 426°C and the TG curve gave an estimated $\text{Ca}(\text{OH})_2$ content of 15.11% (0.76g). Since in cement burning, more than one reaction can occur at a time, the release of combined water from the clay and reaction between CaCO_3 and finely divided quartz may have occurred at 599°C . The endothermic peaks at

636.8°C and 655°C represented the dissociation of MgCO_3 and CaCO_3 . The temperature range of 742.9°C - 862°C and beyond mark the beginning of the formation of calcium silicate and the final product of hydrated CaO , SiO_2 , H_2O (Lea, 1970). The total loss in weight was about 19.6%.



Heating 5%limestone cement, 5%shell cement, 5%pozzolana cement and 5%slag cement revealed dehydration of hydrated calcium silicate, calcium sulphate and ettringite which began at 32°C and ended at 180°C except for 5%slag cement which ended at 202°C. Dehydroxylation of portlandite occurred between 376°C and 488°C whilst CO_2 was released due to decomposition of CaCO_3 at the range of 595°C to 936°C (Taylor, 1997; Dwecket *al*, 2000; Kourouniset *al*, 2007) as given by the equation:



The loss of weight of 5% blended cements due to decomposition of Ca(OH)_2 was between 1.0% and 3.0% compared to 5.9% for the reference cement (Table 5.13). This gives a positive indication that the presence of the four admixtures reduced amount Ca(OH)_2 precipitated as compared to the reference cement and a further proof that addition of the admixtures lowered the portlandite [Ca(OH)_2] content as a result of the dilution of clinker and the pozzolanic reactions that ensued (Vogliset *al* (2005). The total mass loss for heating 5L, 5Sh, 5P and 5S cement mixtures was estimated at 17.73%, 17.25, 15.79 and 16.82% respectively. Further analysis of 5%limestone5%pozzolana cement (ternary blend); 2.5%pozzolana2.5%limestone2.5slag cement and 5%limestone5%pozzolana5%slag

cement (quaternary blend) and 2.5%pozzolana5%limestone2.5%shell2.5%slag cement revealed a further decrease of portlandite to 2.63%, 1.20%, 1.52% and 1.55% respectively. Figure 6.1 clearly shows that the presence of the admixtures significantly reduced the portlandite content from 24.58% in Portland cement to 5.02% in quaternary blend (2.5x2.5y2.5z) and 6.31%-6.46% in quinternary blended cement samples.

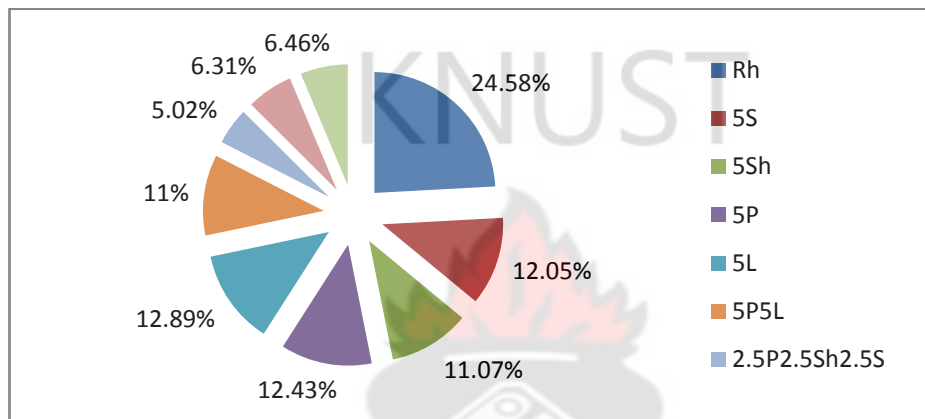


Figure 6.1: Estimated portlandite content in cement samples from TG analysis

6.3.5 Significant results from the mineralogical analysis

Several studies by prominent researchers such Tsakiridis *et al* (2008), Kumar *et al* (2008), Kourounis *et al* (2007), AmitRai *et al* (2002), Monshi and Asgarani (1999), Dongxue (1997), Conjeaud *et al* (1981) among others have used steel slag either alone or in combination with limestone or fly ash as ingredients in cement production. Most slag used was of high CaO composition ranging from 35% to 42% and high C_3S that are very essential for cement hydration and strength development. In this study however, steel slag with low Ca-containing mineral phases content of 12.44% and high wustite (Fe_2O_3) content of 31.52% was used in combination with limestone/clam shells ($CaCO_3$ -based) and clay pozzolana, and

analysed mineralogically to indicate their effect on cement hydration and formation of ettringite and portlandite.

The study has shown that the presence of these admixtures provided unique cement qualities such as low Ca(OH)_2 content and improved impermeability of concrete. The Infrared Analysis showed a shifting of the characteristic $\nu_3\text{SiO}_4$; C-S-H from 970cm^{-1} to between 960cm^{-1} and 980cm^{-1} (Tables 5. 10 and 5.11) when the admixture content was increased from binary to ternary indicating the accelerating effect of admixtures on hydration. This effect is expected to manifest in high early strength of the blended cement, especially the CaCO_3 -based blended cement samples. The ettringite and monosulphonate of CaCO_3 -based admixtures (that is, limestone and shell cement) bands were almost flat or disappeared compared to others, indicating increased reactivity between CO_3^{2-} and SiO_4^{4-} ions.

One important and new finding from the study is that a combination of three (5% each) or all the four admixtures (2.5% each) in the cement almost eliminated portlandite as a result of admixture hydration reactions as obtained from the XRD analysis as presented in Table 5.11. This is a novel revelation and it was sufficiently corroborated by the EDX and TG/DTA analysis. It is also very significant because the near absence of Ca(OH)_2 makes concrete very less susceptible to acidic attack and structural deterioration.

6.4. Compressive Strength

6.4.1 Mortar tests

The results of the mortar compressive strengths of the reference and blended cements with different admixture contents are given in Table 5.15 and 5.16.

Generally, the 2- and 7-day compressive strengths of all the blended cement mortars were higher than the standard minimum value of 10MPa and 16MPa respectively stipulated by EN 197-1 (2000). For the 5% binary blended cements, the 2-day strengths were higher than 19 MPa in all cases, with limestone cement recording the highest value of about 23MPa. The high 2-days and 7-days strengths of the 5% and 10% cement replacement were due to the filler effect of admixtures as a result of the increased surface area that leads to an initial accelerating effect on cement hydration. (Péra *et al*, 1999, Soroka and Setter, 1977). At 28 days, they recorded strengths between 42MPa and 43MPa.

Thus, the cements containing 5% of any of the admixture can be classified as Class 32.5R and 42.5N (EN 197-1). The 28-day strengths of the blended cements ranged between 86.5% and 99.5% of the reference cement, more than 75% stipulated by ASTM C 618 (2008). This means that all the admixtures are very good materials for blending and/or integration in cement for all types of housing construction and are, therefore, suitable for early high-strength cement products as stipulated by EN 197-1 (2000).

The strength development of the various cement mortars from 2 days to 365 days, are presented in Figs. 6.2 whilst the 28-day compressive strengths are given in Fig. 6.3.

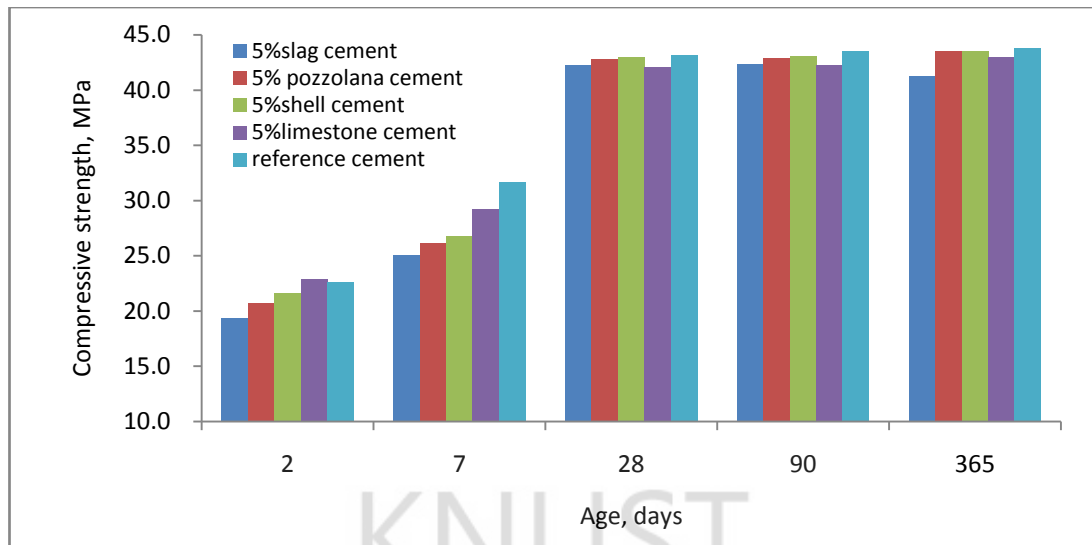


Figure 6.2: Compressive strengths of binary blended cement mortars containing 5% of one admixture.

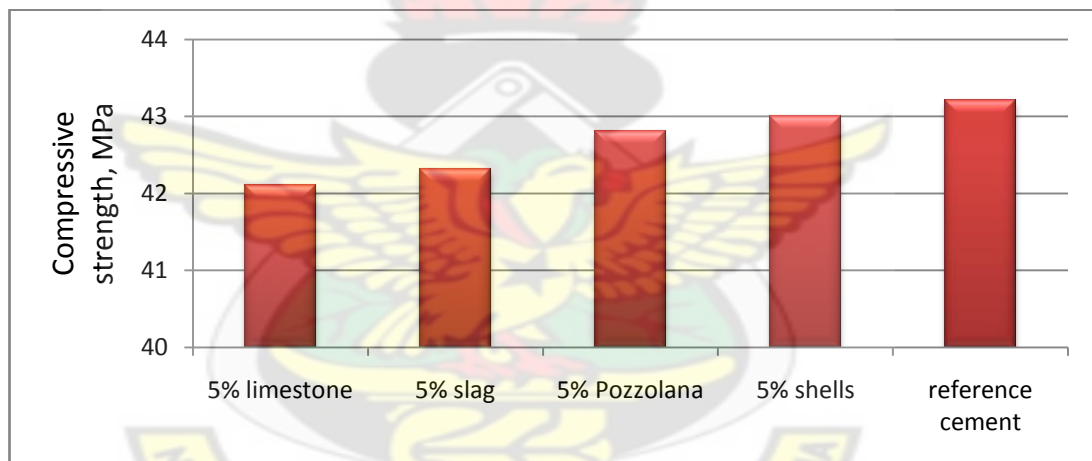


Figure 6.3: 28-day compressive strengths of binary blended cement mortars containing 5% of one admixture

The graphs show that the strengths of the blended samples increased at all times up to 365 days. However, the strengths of the 5% blended cements were always lower than that of reference cement. This is attributed partly to the fact that admixtures normally reduce the rate of reaction thus reducing the heat of hydration. The advantage however is that expansion and shrinkage are reduced resulting in less thermal cracks in cement concrete products (Lea, 1970).

Replacing 10% of the reference cement with 5% each of any two of the admixtures (for example, 5%slag5%shell cement) produced 2-day strengths lower than the 5% cements but higher than 10MPa, ranging between 16.5MPa and 21.5MPa. Fig. 6.4 gives a graphical presentation of strength development of 5%x5%y cements from 2 to 365 days. Pozzolana slag cement produced the highest 28-day compressive strength of 41.83MPa. This could be attributed to the additional silica, CaO, C₂S provided by the two admixtures. The lowest strength of 40.1MPa was produced by limestone shell cement.

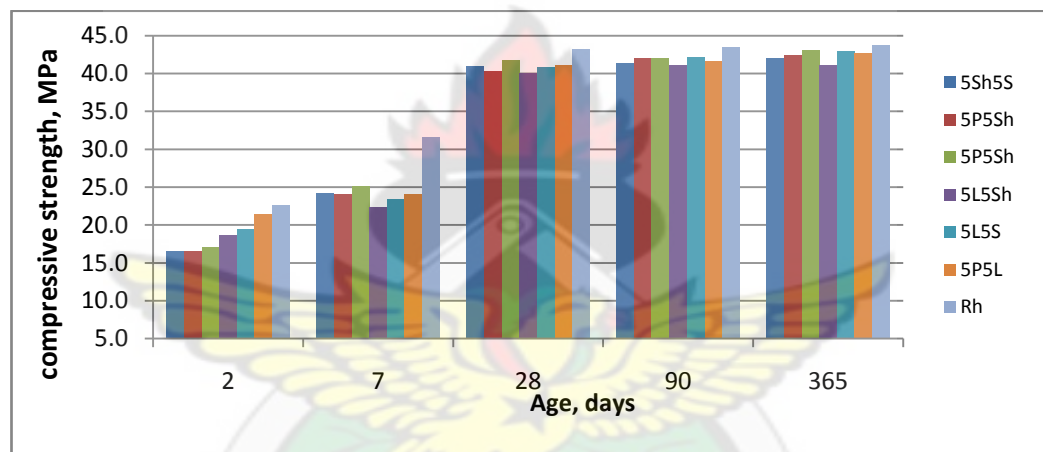


Figure 6.4: Compressive strengths of ternary blended cements containing 5% each of two admixtures.

Fig. 6.5 illustrates the compressive strengths development of 10%x5%y and 5%x10%y (e.g. 10%pozzolana5%limestone) blended cements at 2, 7, 28, 90 and 365 days. The 2-day values were above 14 MPa whilst the 28-day strengths were between 38.5MPa and 40.5MPa (also presented in Table 5.14). These cements are classified as CEM II Class 32N (EN 197-1) and can be improved to Class 32.5R and 42.5N when the mineral admixtures are milled finer to increase their surface area. Class 32N type can be used for plain and reinforced concrete works, block making, bonding and rendering. The results, however, show that ordinary Portland cement

can be replaced with 15% of admixtures ($10\% \times 5\%y$; $5\% \times 10\%y$) for both concrete and general construction. For the strength characteristics of 15% replacement of ordinary Portland cement, it is observed that even though the 2-day strength of $10\% \times 5\%y$ cements (ternary blend) were higher than $5\% \times 5\%y5\%z$ cements (quaternary blend) the 28-day and 365-day compressive strengths were almost the same (Fig. 6.5; Fig. 6.6).

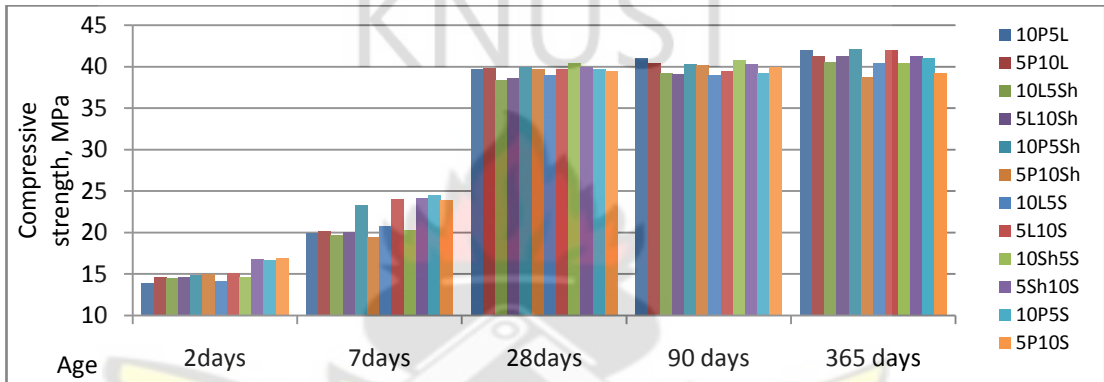


Figure 6.5: Compressive strengths of ternary blended cements containing $10\% \times 5\%y$ or $5\% \times 10\%y$ admixtures

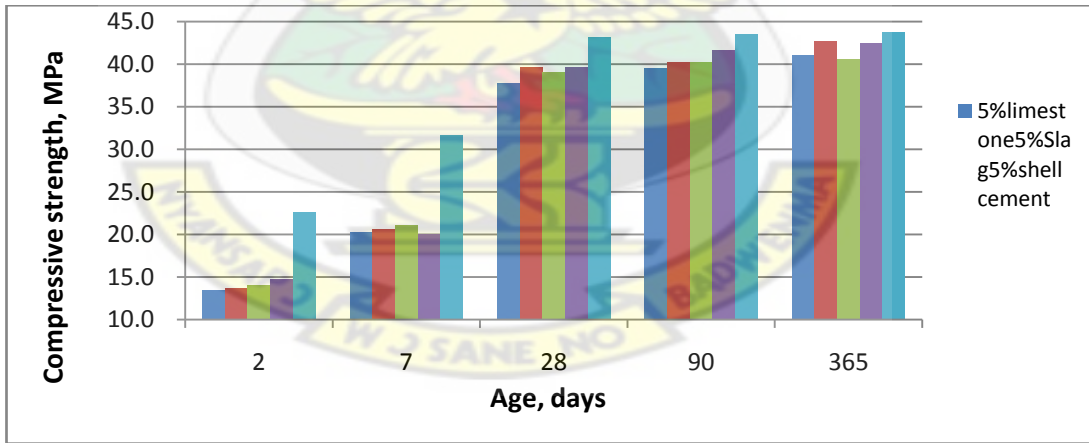


Figure 6.6: Compressive strengths of quaternary blended cements containing 5% each of three admixtures

At 15% to 20% replacement, the filler effect is surpassed by the dilution effect and this leads to lower relative strength as compared to up to 10% replacement. The

compressive strength development of 20% blended cement that had been replaced with 10% each of two admixtures (10% $\times$ 10%) is illustrated in Fig. 6.7. The strengths at 2 days averaged 13.8MPa whilst the 28-day strengths were above 38MPa but below 40MPa. The strengths with 20% replacement were always lower than that of 5% and 10% (5% $\times$ 5%) and this should be attributed to reduction of active clinker minerals needed to obtain early high strength and slow pozzolanic action as stated by Wild *et al* (2001). The 10%pozzolana10%limestone 2- and 28-day strengths of 13.9MPa and 38.0MPa respectively compared with 12.9MPa and 41.4MPa obtained by Ghrici *et al* (2010). Also, the strengths obtained from 10% slag content with additional 10% content from any of the admixtures ranged between 87% and 91.5% as compared to 75% and 80% obtained by Altun and Yilmaz (2002) and Kourounis *et al* (2007).

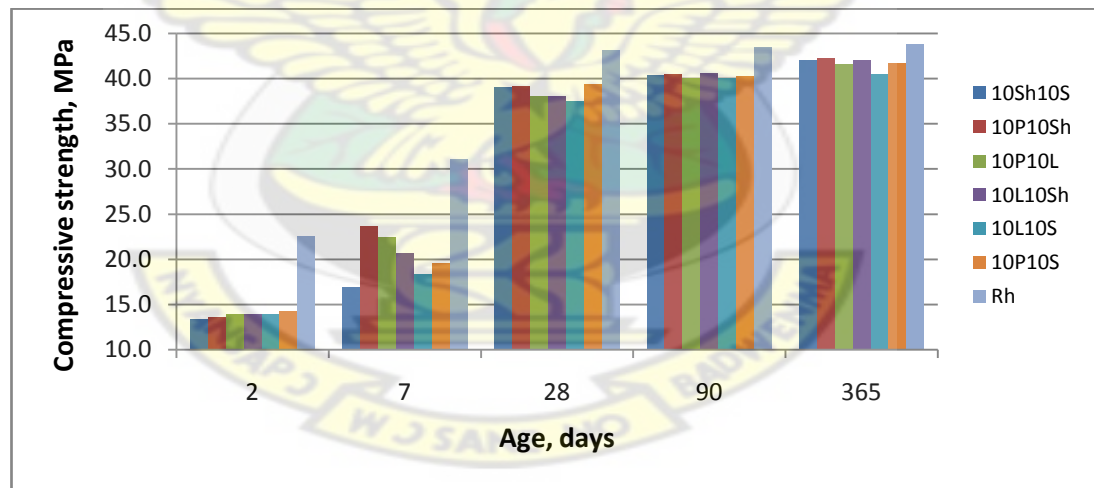


Figure 6.7: Compressive strengths of ternary blended cements containing 10% each of two admixtures

This means that these blends could not be considered as early high strength cements for high strength concrete structures but are suitable for low to medium strength concrete and general construction. Pozzolana slag cement gave the highest strength

of 39.4MPa while slag limestone produced the minimum of 37.5 N/mm². The results obtained by replacing 20% cement by 5% each of the four admixtures show that the compressive strengths at 2days were higher (15.1 N/mm²) than that obtained from 10% $\times$ 10% $\times$ y and 5% $\times$ 5% $\times$ y5% $\times$ z cements (Table 4.13). The strength of 38.7 MPa obtained at 28 days (almost the same as for 10% $\times$ 5% $\times$ y and 5% $\times$ 5% $\times$ y5% $\times$ z replacements) makes the blended cement (using all the four admixtures) suitable for medium strength concrete and general construction.

The results also show that integrating 7.5% of the admixtures by using 2.5% each of three of the admixtures gave almost the same strength as replacement of cement by 5% admixture at 28 days (average 42.0MPa) and about 97.3% of that of reference cement. However, the 2-day strengths of 5% binary cements averaged higher than 20N/mm² whereas those of 2.5% $\times$ 2.5% $\times$ y2.5% $\times$ z averaged below 19N/mm². Increasing the admixture content to 20% with 5% each of the four admixtures produced relatively low early strength of 15.1MPa at 2ays and 28-day strength of 38.1MPa (Fig. 6.8).

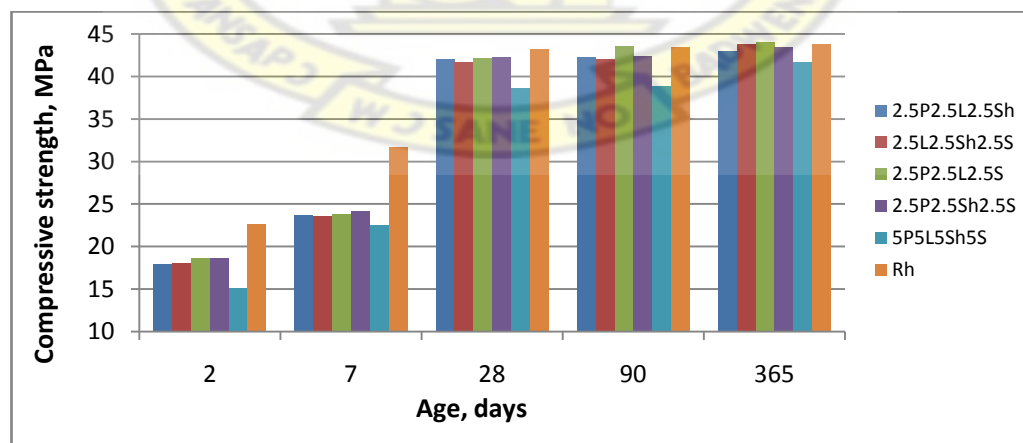


Figure 6.8: Compressive strengths of quaternary and quinary blended cements

6.4.2 Concrete Tests

The effect of blended cements on the fluidity of concrete was determined by slump test. The results are presented in Table 5.20. Concretes made with partial replacement of ordinary Portland cement by 5% admixtures exhibited enhanced workability compared of the reference mix, except pozzolana cement using w/c ratio of 0.6. The highest slump was recorded with mixtures containing shell cement. On the other hand, concretes made with pozzolana showed decrease in workability. The decrease in slump of pozzolana concrete could be attributed to the greater surface area due to relatively lower specific gravity of 2.59 of pozzolana. Binary blends with ordinary Portland cement with 5% each demonstrated lower slump in all the fresh concrete mixes with pozzolana. Similar results were observed with ternary and higher blends. It was generally noticed that fresh properties of blended concretes without pozzolana showed an equal or improved workability in relation to reference mix. This was in agreement with results obtained by Abdullahi (2009), Adesanya *et al* (2009) and Lea (1970) that incorporating pozzolana in concrete usually has a rather lower slump at the same water content. All concrete mixtures were found to be cohesive, relatively workable and showed no tendency of segregation.

The mechanical properties as compressive strength of blended concretes were evaluated at 2, 7, 28, 90 and 365 days of curing. Table 5.20 show the compressive strength result obtained from cylindrical specimens using a water cement ratio of 0.6 and these are presented graphically in Figs. 6.9 – 6.13. The strengths obtained for 5%*x* and 2.5%*x*2.5%*y*2.5%*z* were higher than the standard value of 20 MPa and at least 91.6% of the reference cement. 5%shell cement gave the highest strength of 21.5MPa compared to a value of 22.5MPa for the reference cement

whereas 5% slag cement provided the least strength of 17.2MPa (about 76.4% of control). These results compared favourably with the ASTM C 618 (2008) specification which stipulates minimum 28-day strength of 75% of the reference.

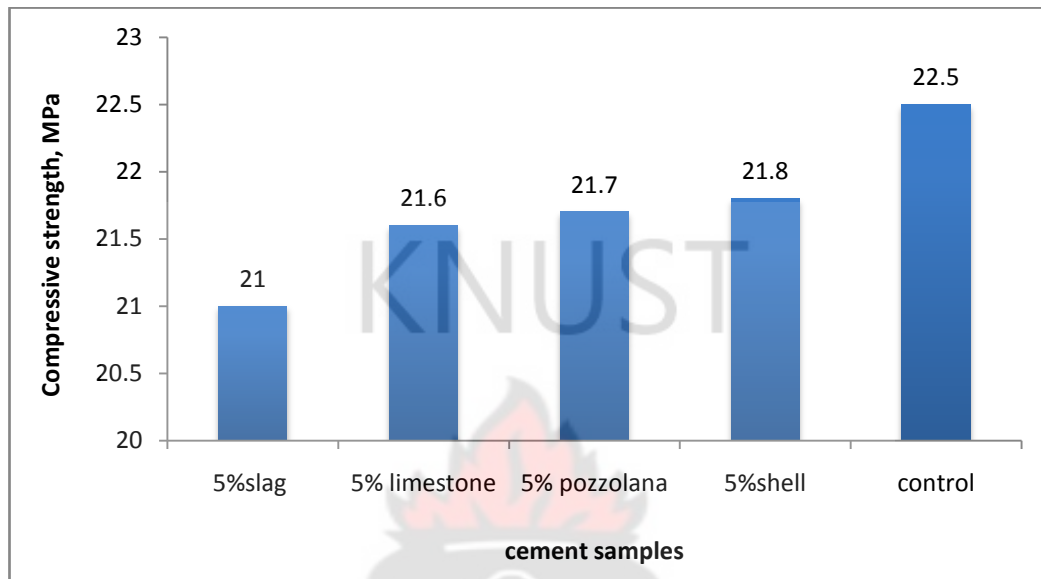


Figure 6.9: 28-day Compressive strengths of 5% binary blended cement 1:2:4 concrete cylinders

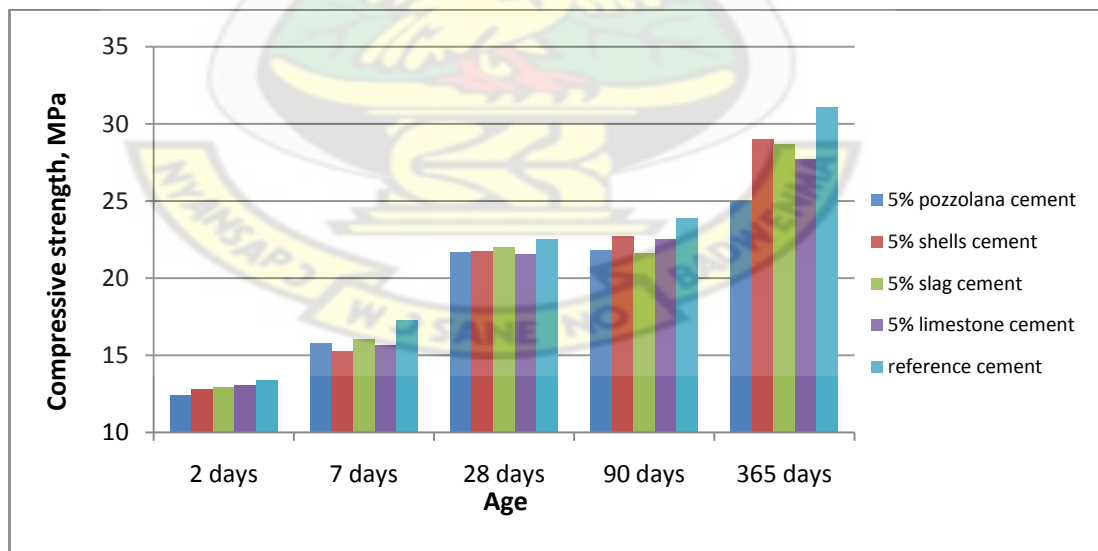


Figure 6.10: Compressive strengths of 5% binary blended cement 1:2:4 concrete cylinders

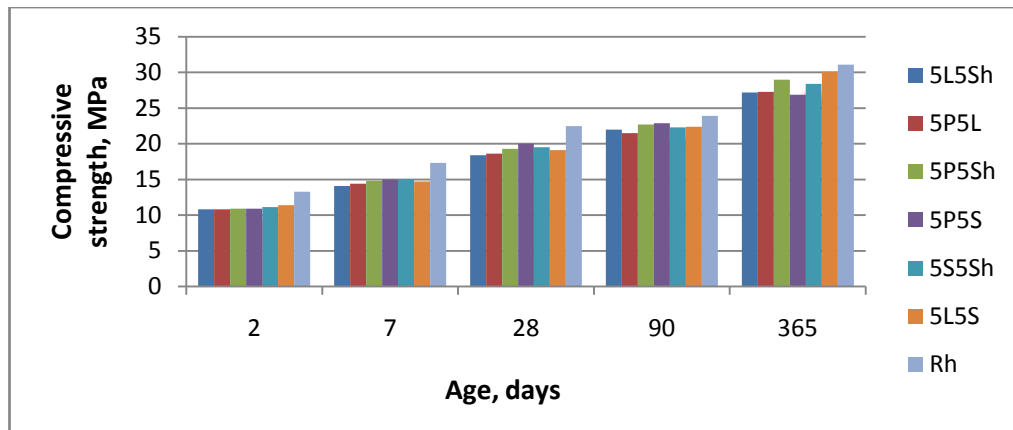


Figure 6.11: Compressive strengths of 5% x 5% ternary blended cement 1:2:4 concrete cylinder

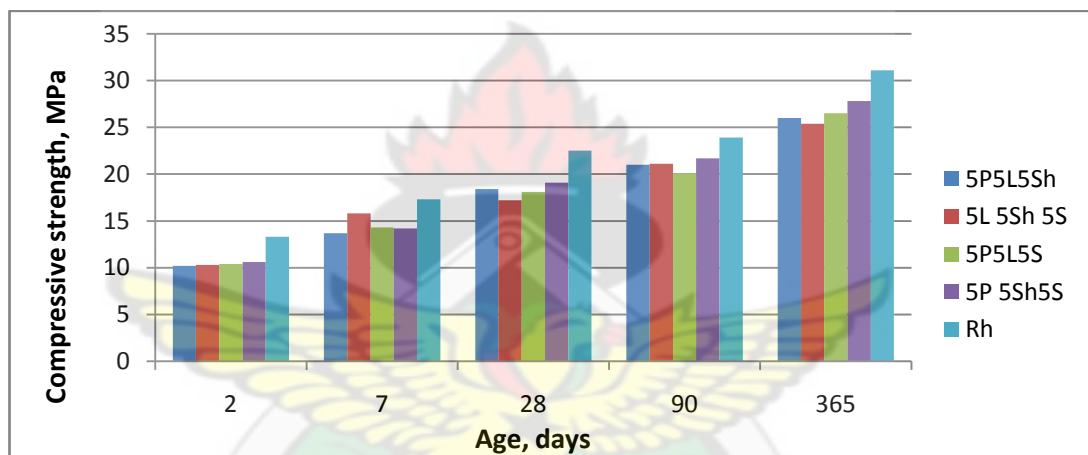


Figure 6.12: Compressive strengths of quaternary (5% x 5% y 5z) blended 1:2:4 concrete cylinder

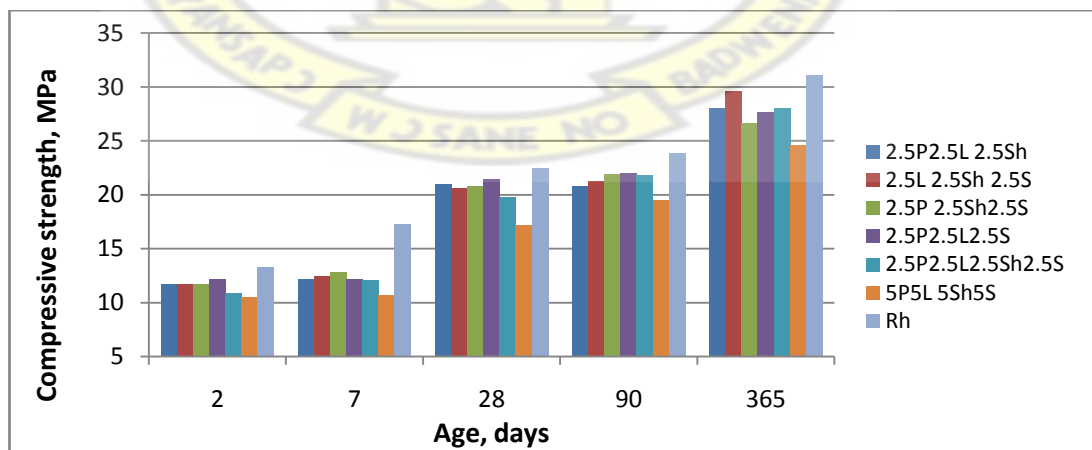


Figure 6.13: Compressive strengths of quintenary blended 1:2:4 concrete samples

The strength of the concrete increased between 1% and 19% when the water cement ratio was reduced to 0.55. However, working with the concrete was more difficult even though the slump values also improved. Strengths ranging from 19.1MPa to 24.6MPa were obtained and the highest strength came from 5%pozzolana cement.

6.5 Flexural Tensile strength

The flexural strength is a measure of an unreinforced concrete beam or slab to resist failure in bending. It may also be referred to as modulus of rupture (Dayaratnam, 2006). The tensile strength of the concrete is usually between 10 and 20% of its compressive strength (Neville, 2000). The results obtained from the tests on the blended and reference cements indicated that replacing cement with 5% of the admixture did not affect the flexural strength of the concrete. For concretes with water-cement ratio of 0.5%, the flexural tensile strengths were between 18.0% and 24.29% of the 28-day compressive strengths of the concrete (Table 5.21).

Replacing cement with 5% admixtures using both water-cement ratio of 0.55 and 0.6 did not reduce the tensile strength significantly. The trend however shows that increasing the admixture content to 15% reduced the flexural strength by between 11% and 20%, with the exception of 5%pozzolana5%limestone, 2.5%limestone2.5%shell2.5%Slag and 2.5%pozzolana2.5%limestone2.5%shell cements that gave the same strength as the control (Figs 6.14 and 6.15) as reported by Carrasco *et al* (2004) using limestone and blast furnace slag admixtures. Significantly, replacing cement with 2.5% of each of four admixtures produced high flexural tensile that was higher than for CEM I Class 42.5N cement. The tensile strengths obtained for the blended cement ranged between 21% and 53% of

compressive strengths compared to 10% - 20% stipulated by standards (Neville, 1996). Compared to results of $w/c = 0.55$, the results were always higher than that of 0.6. This is attributed to effect of dilution by water which reduces the strength of concrete.

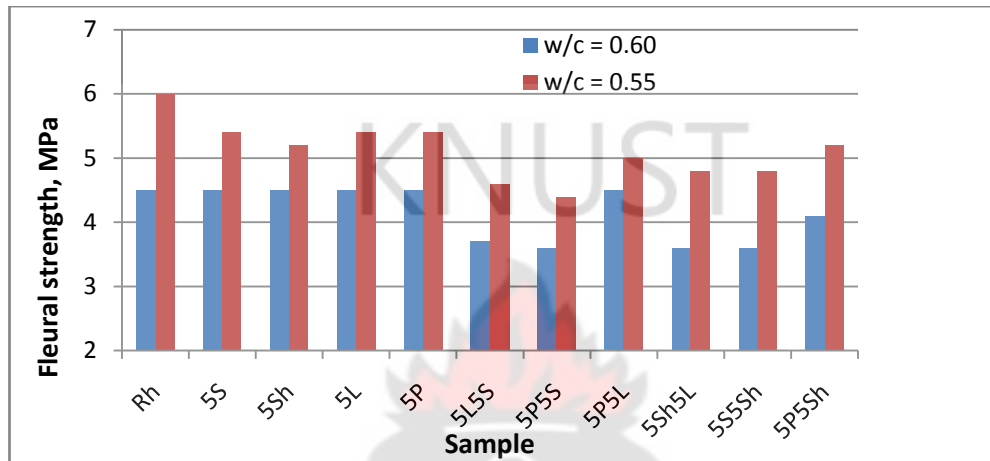


Figure 6.14: Flexural strength of binary and ternary concrete at 28 days

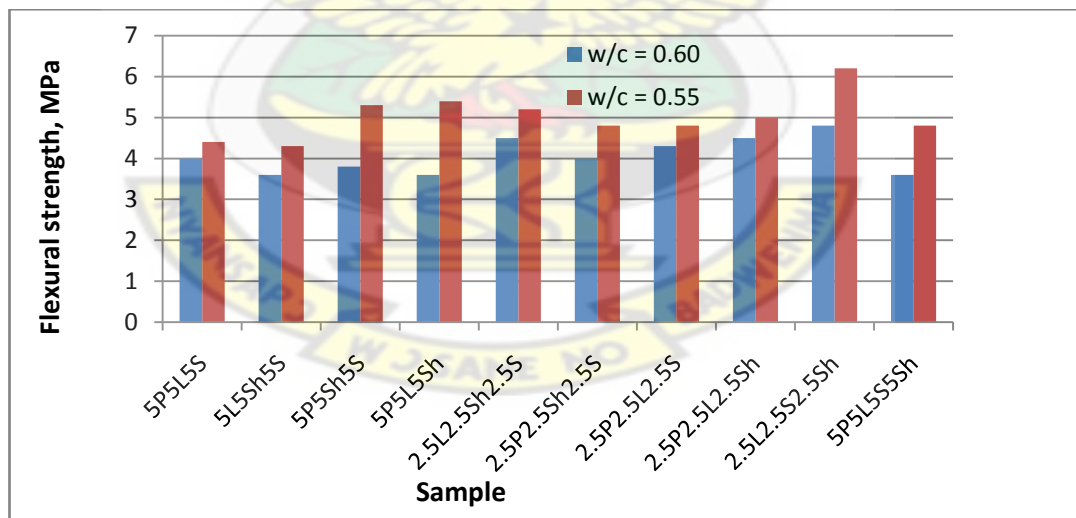


Figure 6.15: Flexural strength of quaternary and quinternary concrete at 28 days

6.6 Durability tests

6.6.1 Sulphate and chloride resisting test

Mortar cubes, produced according to EN 196-1, were immersed in 5% Na_2SO_4 solutions and sea water (NaCl). The cubes were examined visually, photographed and tested for compressive strength at 28, 180 and 365 days. Figs. 6.16–6.19 show the physical appearance of the mortar cubes in sodium sulphate solution and seawater after 28 and 365 days. The samples seemed not physically affected, as there were no visible signs of deterioration.

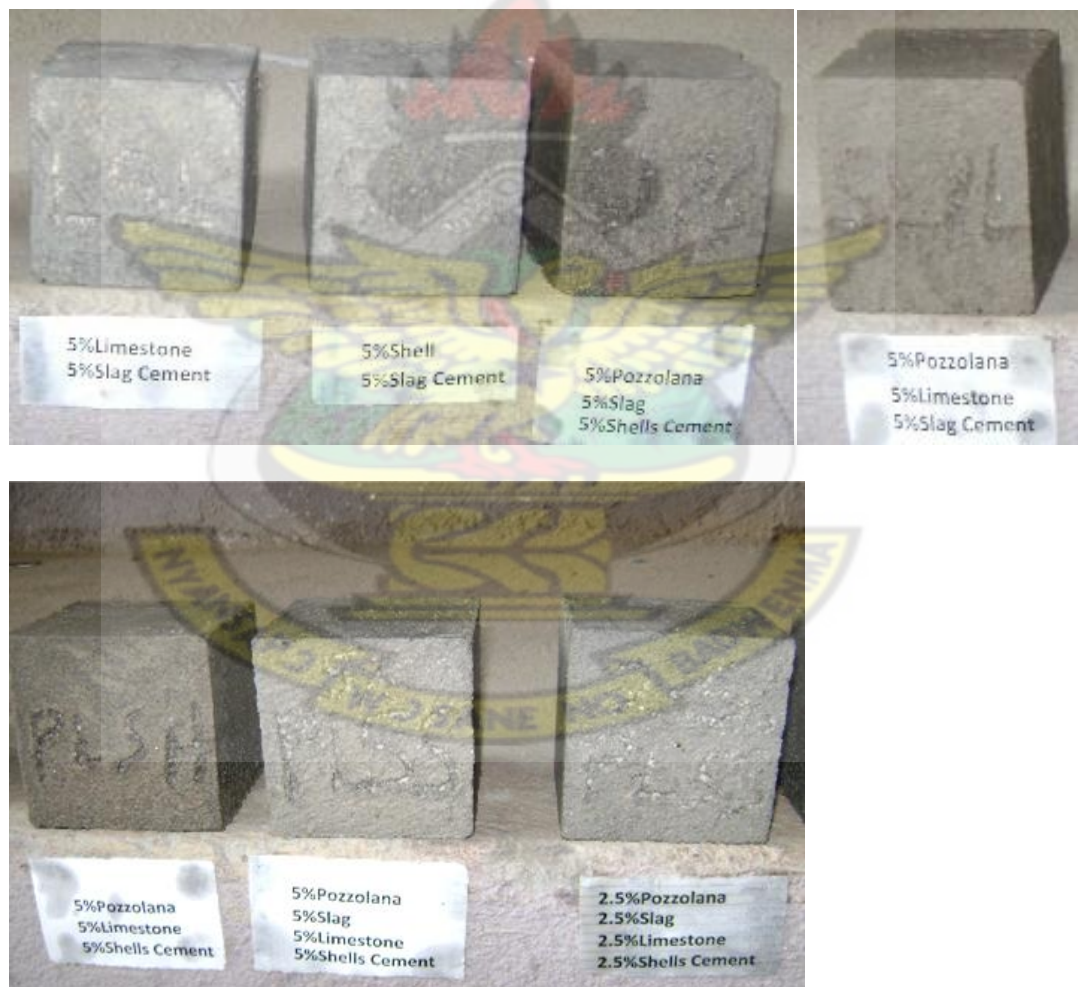


Figure 6.16: Appearance of mortar cubes after 28 days in Na_2SO_4 solution



Control and 5%x blended cement cubes



Figure 6.17: Appearance of blended mortar cubes after 28 days in seawater

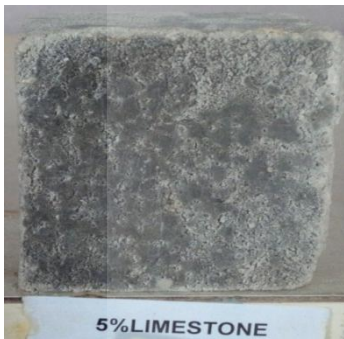
SEA WATER



5% Na₂SO₄



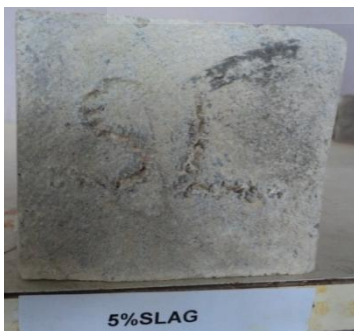
Portland cement



5% limestone cement



5% shell cement



5% slag cement

Figure 6.18: The state of control and 5% x cement cubes after a year in seawater (left) and Na_2SO_4 solution (right)



Figure 6.19: The state of the cubes after a year in seawater (left) and NaSO_4 solution (right)

Analysis of their compressive strengths at 28 days presented a decrease of 8% to 36% in seawater (NaCl) with 5%shell and 5%limestone being most affected. 5%slag cement produced the highest strength of 35.6MPa, compared to 32.2MPa of the control, whilst 5%shell cement gave the least value of 27.3MPa in seawater. The decrease in strength in the sulphate solution was between 8% and 42% but in this case, 5%slag cement was

most affected. 5%pozzolana5%shell cement gave the best result of 38.8MPa compared to 33.1MPa from oPc(Figs. 6.20).

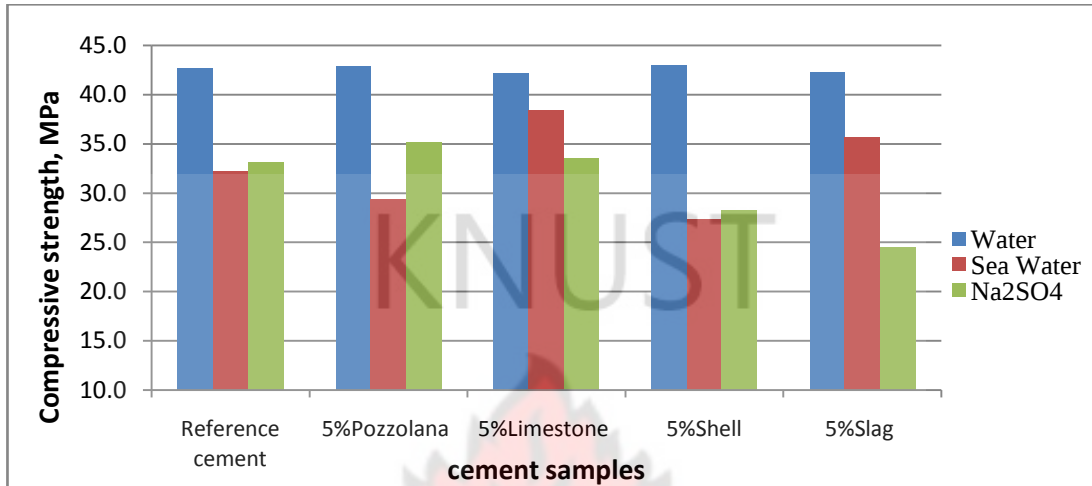


Figure 6.20: Compressive strengths of 5% cement mortars in water, seawater and 5%Na₂SO₄solution at 28 days

Generally, slag blended cements exhibited better resistance to chloride attacks and this is because slag increased the alkalinity of the pore solution of cement solution as the hydration reaction proceeded. This prevented the diffusion of chloride ions thus providing good protection (Benjamin, 2000). Also, the effect of seawater (NaCl) was reduced as the number of admixtures in the cement were increased (Fig. 6.21).

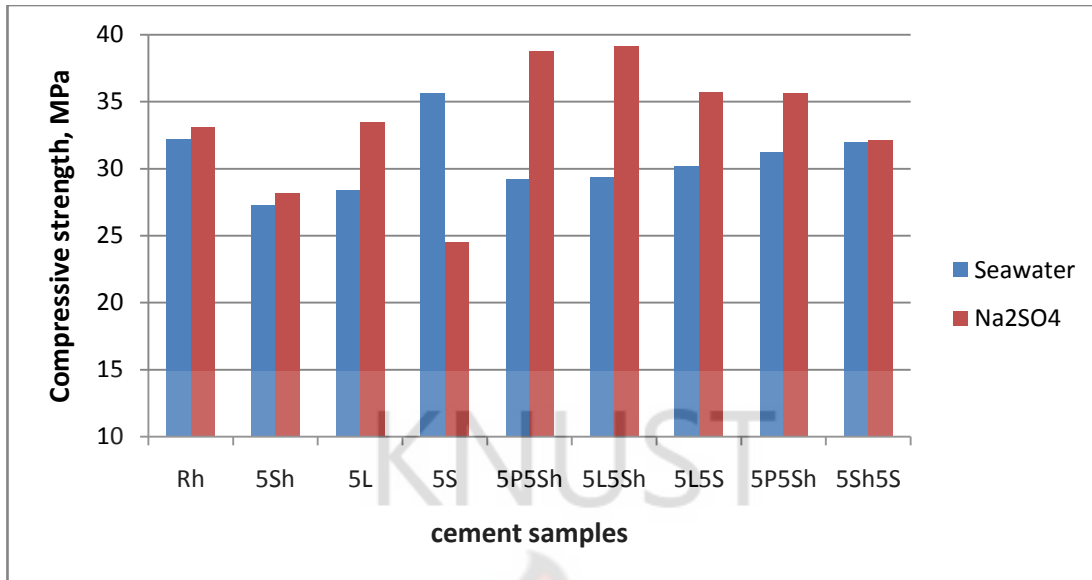


Fig. 6.21: Compressive strength of blended cement mortars in water, seawater 5% Na₂SO₄ solution at 28 days.

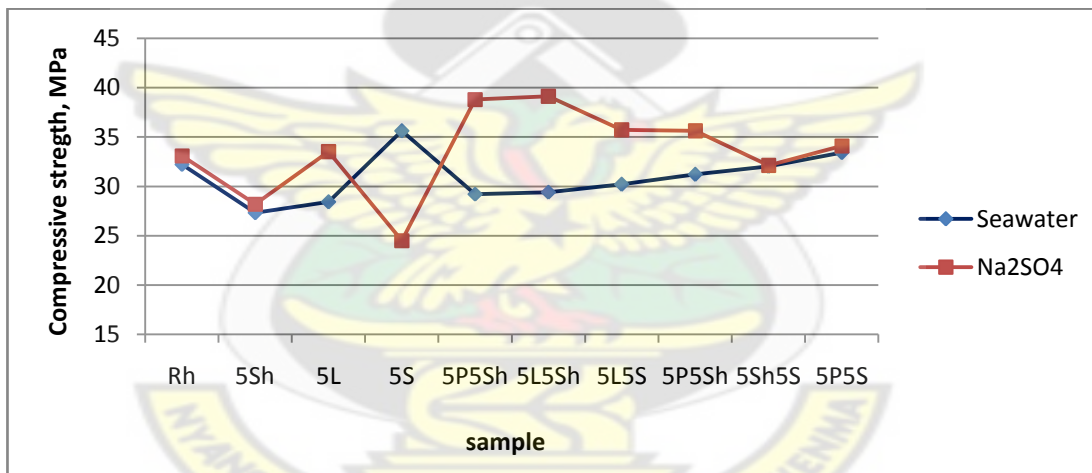


Figure 6.22: Comparative compressive strengths of binary and ternary blended cement mortars in seawater and 5%Na₂SO₄solution at 28 days

The effect of 5%Na₂SO₄ solution was more pronounced than seawater. This deleterious effect was due to the attack of sulphate on Ca(OH)₂ and alumina producing ettringite and other sulphonate compounds which lead to expansion of concrete/mortar and disruption. The results (Table 5.18) show that pozzolana-based cement produced the

highest resistance to sulphate attack with 5%slag cement giving the lowest strength value of 24.5MPa. The low CaO/SiO₂ ratio of the clay pozzolana accounted for its effective sulphate resistance (Farrelet *al*, 2000). Significantly, increasing the admixture content from binary to quinary improved the resistance to sulphate attack. This could be attributed to the combined effect of admixture filling pores, pozzolanic action and reduction of Ca(OH)₂, and reduction of alkalinity needed for sulphate action. In all, 2.5%*x*2.5%*y*2.5%*z*2.5%*p* cement provided the best blend that could resist both seawater and sulphate solution negative action. This further confirms the assertion that a combination of four of the admixtures at 2.5% each reduces the portlandite content from the X-ray analysis (Table 5.11) and TG analysis (Table 5. 13) of the cement and such will provide high resistance to acidic attack.

Figure 6.18 and 6.19 show that the physical appearance of the mortar cubes in both solutions deteriorated and the strengths also decreased(Fig. 6.22) after 365 days.In both NaCl and 5% Na₂SO₄solutions, 5%limestone5%shell cement was most affected by as much as 35% and 39% respectively. As usual, blending three or more admixtures produced cements which performed better than the reference cement (Figs. 6.22 – 6.23). Finally, slag blended cements performed better than the rest in both solutions as stated by Wu *et al*,(1999) and Dongxue*et al*,(1997) in their work on resistance of slag cement in sulphate solution.

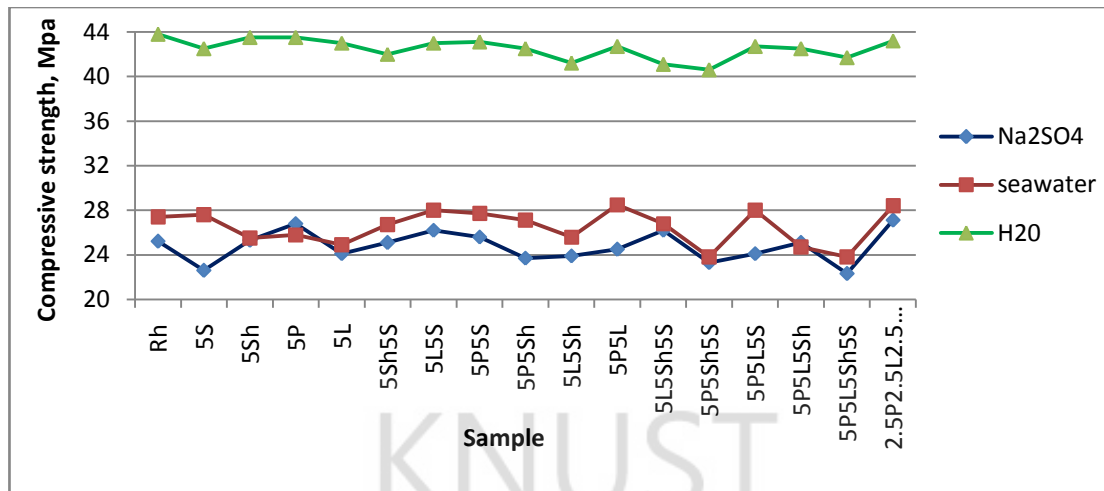


Figure 6.23: Compressive strengths of cement mortars in various solutions at 365 days

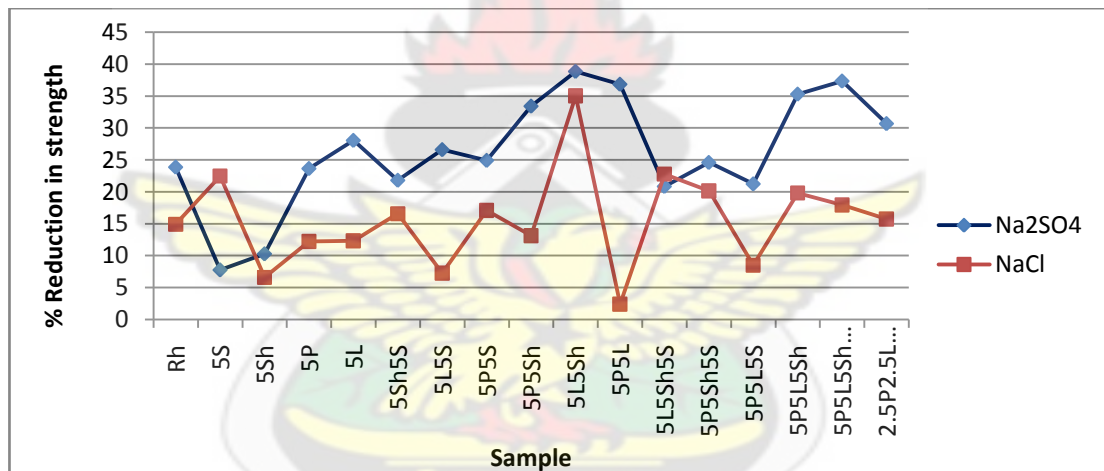


Figure 6.24: Percentage reduction of strength of blended cement mortars in seawater and Na₂SO₄ solution in 365 days

6.8 Economic benefits on using admixtures

Cement consumption in Ghana has been increasing steadily from 1.81 million tonnes in 2000 to about 3.4 million tonnes in 2010. Concurrently, the price of cement has increased from GH¢3.2 to GH¢10 - 12.00 during the same period. The current cement price ranges from to GH¢12.00 to GH¢16 (the year 2011) depending on the geographic location and the reasons for such trend have been enumerated in Chapter One. In addition, about 85% cement ingredients are imported into Ghana.

Assuming an estimated 3.4 million tonnes of cement consumed in Ghana, with a 5% of loss during handling and milling, the following cost saving analysis is made for admixture blended cement:

$$\text{Total clinker import} = 3.4 \times 10^6 \times 0.95 \times 1.05$$

$$= 3.3915 \times 10^6 \text{ tonnes}$$

$$\text{Assuming an FOB price} = \$62.00/\text{tonne}$$

$$\text{Total cost of clinker} = \$210.27 \text{ million}$$

$$\text{Handling cost} = 1\% \text{ of FOB}$$

$$= \$2.10 \text{ million}$$

$$\text{Import Duty, VAT etc} = 5\%$$

$$= \$10.51 \text{ million}$$

$$\text{Total cost (excluding insurance)} = \$222.89 \text{ million}$$

Replacing at least 15% of total clinker imports by these admixtures would amount to a

$$\text{capital saving of} = \$222.89 \times 0.15 \text{ million}$$

$$= \$33.43 \text{ million}$$

This will be the least capital savings to Ghana per annum. In addition, the use of suitable local admixtures in cement production in Ghana will provide the following benefits:

- Increase utilization of local materials in cement production;
- Provide cheaper but durable cement for the construction industry;

- Reduce global environmental pollution; especially in the area of carbon credit;
- Increase housing delivery in terms of cost, and
- Provide revenue to the state and local authorities.

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CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS

7.0 Conclusions

Locally available limestone, clam shell, clay and steel slag were used as admixtures and studied to ascertain their influence on cement hydration and properties. Physical and chemical tests were performed on the four admixtures as well as cement blended with these admixtures. Binary, ternary, quaternary and quinary cement blends were prepared for physical, chemical, mineralogical and mechanical properties. Also, durability tests were performed to determine their resistance to acidic water.

The soundness of the blended cement samples were less than 2.0mm. The water demand of the blended cements ranged from 24.5% to 34.5% and that it increased as the percentage admixture replacements of cement increased. However, 5% slag cement was lower than that of reference cement. The initial setting times of 5% and 5%x5%y blended binary and ternary cements were lower than reference cement but increasing admixture content increased the setting times. The initial and final setting times of all cement blends were within the standard minimum limits (GS 22). The slag containing cements normally demanded less water than the rest.

Infrared spectrometry, X-ray diffraction, SEM/EDX and TG/DTA analysis showed clearly that the presence of the four admixtures in concrete provided unique cement qualities such as low Ca(OH)_2 content and improved impermeability of the concrete.

The Infrared analysis showed a shifting of the characteristic $\nu_3\text{SiO}_4$; C-S-H from 970cm^{-1} to between 960cm^{-1} and 980cm^{-1} when the admixture content was increased from binary to ternary indicating the accelerating effect of admixtures on hydration. This effect manifested in high early strength of the blended cement, especially the CaCO_3 -based blended cement samples. The ettringite and monosulphonate of CaCO_3 -based admixtures (that is, limestone and shell cement) bands were almost flat or disappeared compared to others, indicating increased reactivity between CO_3^{2-} and SiO_4^{4-} ions.

One significant and new finding from the study is that a combination of three admixtures (5% each) or all four admixtures (2.5% each) in the cement almost eliminated portlandite content as compared to 36.9% in the reference cement as a result of admixture hydration reactions as shown clearly from the XRD analysis. This is a novel revelation and it was sufficiently corroborated by the EDX and TG/DTA analysis. It is also very significant because the near absence of $\text{Ca}(\text{OH})_2$ will make concretes made from these blended cements less susceptible to severe acidic attack and structural deterioration. The EDX and X-ray analysis also showed increased silica and oxygen composition of the blended cement compared to the control indicating increasing amounts of calcium silicate components.

All the 5%*x* blended cements produced high 2- and 28-day strengths which classified them as CEM I Class 42.5N cement whilst 5%*x*5%*y* and 2.5%*x*2.5%*y*2.5%*z* and 2.5%*x*2.5%*y*2.5%*z*2.5%*p* cement yielded CEM II/A Class 42.5N cements according to EN 197-1 standards, suitable for high strength concrete construction. All the other blended

cements are classified as CEM II/A Class 32.5R cement, except 5%*x*5%*y*%5*z*5%*p* cement. The concrete tests revealed that 5%*x* blended cement concretes exhibited better workability than the reference cement and

also the compressive strengths of all the 1:2:4 blended cement concretes were higher than the targeted value of 20MPa. It is expected that 1:1.5:3 mixes will provide higher strengths. The mechanical properties of the blended cement could be improved when more efficient milling equipment and grinding aids are used, to better inter-grind the cement or clinker with admixtures instead of just blending them.

The durability tests using sea water and 5%Na₂SO₄, showed that the compressive strengths of all the cement samples were affected up to 365 days; the effect of 5%NaSO₄ solution was more pronounced than seawater. Generally, slag blended cements exhibited better resistance to chloride attacks whilst pozzolana-based cements produced the highest resistance to sulphate attack. The study showed that the effect of seawater (NaCl) and Na₂SO₄ on strength was reduced as the number of admixtures in the cement were increased. In all, the quaternary (2.5%*x*2.5%*y*2.5%*z*2.5%*p*) cement provided the best blend that could resist both seawater and sulphate solution negative action. This confirmed the assertion that reduction of the portlandite content as a result of a combination of four admixtures in cement (from the X-ray analysis and TG analysis) will provide high resistance to acidic attack.

Economically, incorporating local admixtures up to 15% of cement content will save the nation at least \$33.43 million annually from clinker imports. In addition, it would

provide increased utilization of local materials in cement production, cheaper but durable cement for the construction industry, reduce global environmental pollution, increase housing delivery in terms of cost, and provide revenue to the state and local authorities.

7.1 RECOMMENDATIONS

From the results and conclusions drawn from the analysis made it is recommended that the limestone, clam shells, clay deposits and the steel slag produced as waste from the steel industries in Ghana be exploited and used as admixtures in cement production in order to improve the mechanical properties of cement products. However, further works need to be done on utilisation of blended cements using a combination of three and four admixtures, for the construction of both ordinary and reinforced concrete structures for observation and evaluation. This will include, among others:

- Pilot production with the ultimate aim of utilising local admixtures in cement must be encouraged.
- Further studies on long-term (5yrs) strength and other properties of blended cements must be carried out.
- Construction of test walls in the three climatic (coastal, tropical and savannah) for field and related studies related to environmental effects must be conducted.

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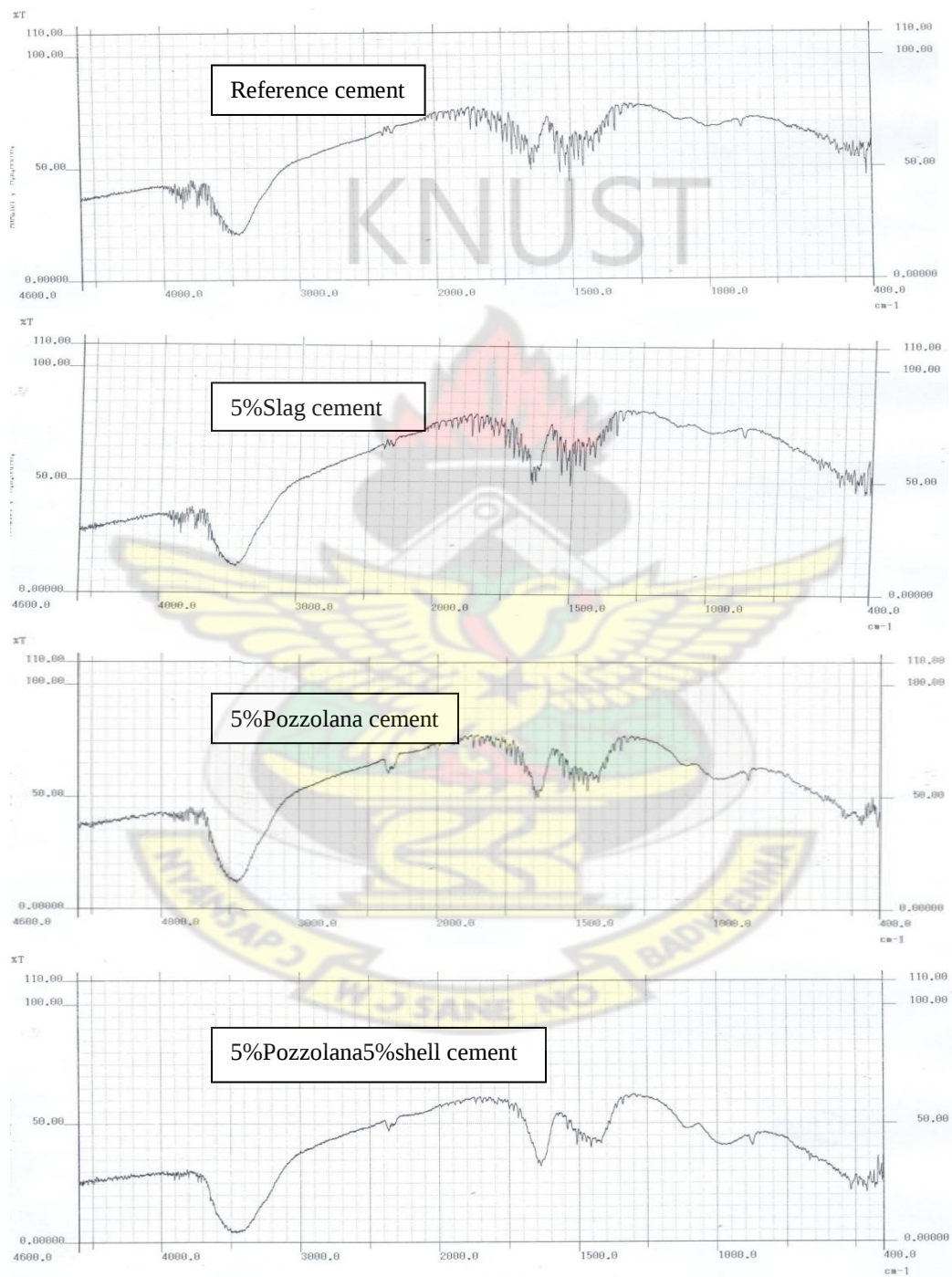
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APPENDICES

APPENDIX I

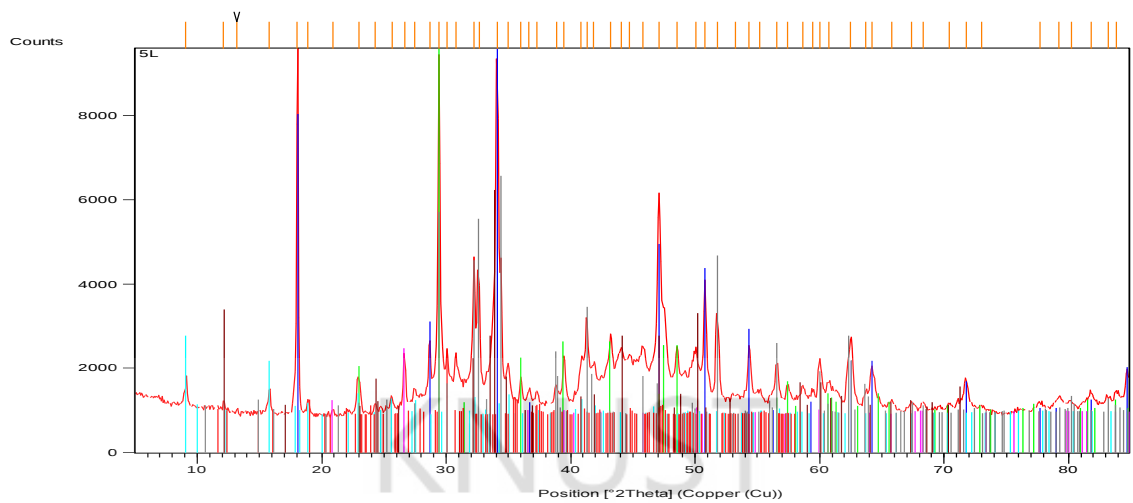
Infrared Spectra of Some Blended Cements



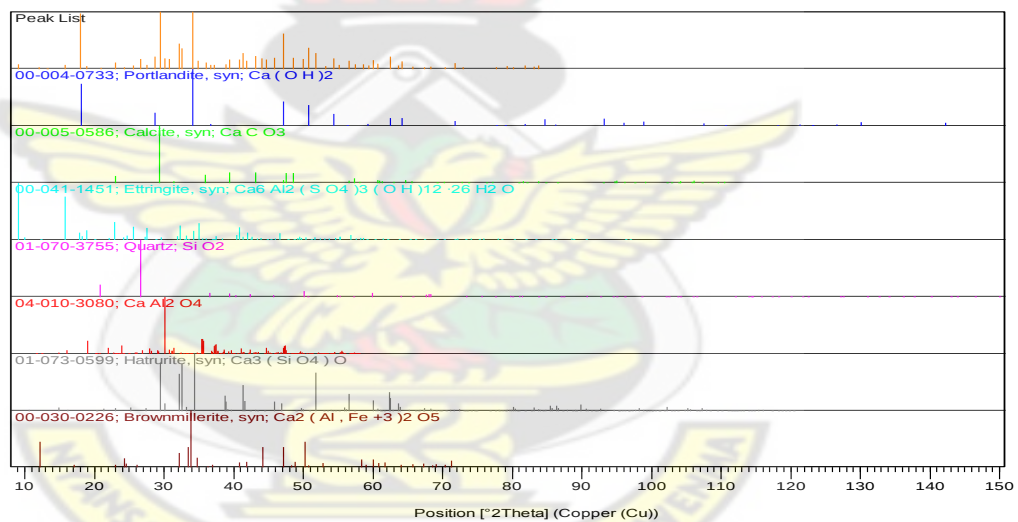
APPENDIX II

XRD Measurement Conditions:

File name	C:\Data 2010\June 2010\Eugene_5L.xrdml
Sample Identification	5L
Comment	5 to 85 deg
Measurement Date / Time	20/06/2010 08:46:10
Operator	Administrator
Raw Data Origin	XRD measurement (*.XRDML)
Scan Axis	Gonio
Start Position [$^{\circ}$ 2Th.]	5.0300
End Position [$^{\circ}$ 2Th.]	84.9500
Step Size [$^{\circ}$ 2Th.]	0.0800
Scan Step Time [s]	10.0000
Scan Type	Continuous
Offset [$^{\circ}$ 2Th.]	0.0000
Divergence Slit Type	Automatic
Irradiated Length [mm]	12.00
Specimen Length [mm]	10.00
Receiving Slit Size [mm]	0.2000
Measurement Temperature [$^{\circ}$ C]	25.00
Anode Material	Cu
K-Alpha1 [$\text{\AA}$]	1.54060
K-Alpha2 [$\text{\AA}$]	1.54443
K-Beta [$\text{\AA}$]	1.39225
K-A2 / K-A1 Ratio	0.50000
Generator Settings	40 mA, 50 kV
Diffractionmeter Type	0000000000000000
Diffractionmeter Number	0
Goniometer Radius [mm]	173.00
Dist. Focus-Diverg. Slit [mm]	100.00
Incident Beam Monochromator	No
Spinning	No



Peak List:



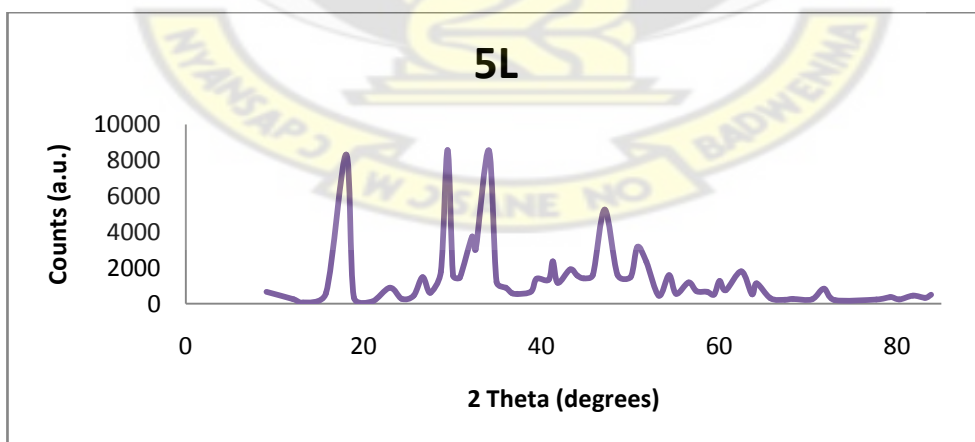
Pattern List:

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-004-0733	55	Portlandite, syn	0.000	1.044	Ca (O H) ₂
*	00-005-0586	42	Calcite, syn	0.000	0.550	Ca C O ₃
*	00-041-1451	31	Ettringite, syn	0.000	0.202	Ca ₆ Al ₂ (S O ₄) ₃ (O H) ₁₂ · 26 H ₂ O
*	01-070-3755	28	Quartz	0.000	0.154	Si O ₂
*	04-010-3080	13	calcium dialuminium oxide	0.000	0.268	Ca Al ₂ O ₄
*	01-073-0599	41	tricalcium silicate oxide	0.000	0.588	Ca ₃ (Si O ₄) O
*	00-030-0226	19	Brownmillerite, syn	0.000	0.344	Ca ₂ (Al , Fe +3) ₂ O ₅

Document History:

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
9.0798	668.15	0.2362	9.73977	7.79
12.1076	253.30	0.2362	7.31009	2.95
13.1908	63.90	0.1574	6.71214	0.75
15.7702	592.38	0.2362	5.61962	6.91
18.0290	8308.53	0.2362	4.92031	96.92
18.9090	359.53	0.2362	4.69327	4.19
20.9076	117.50	0.1574	4.24892	1.37
22.9608	892.86	0.3149	3.87342	10.42
24.3136	266.36	0.1574	3.66088	3.11
25.6265	448.51	0.2362	3.47623	5.23
26.6447	1475.01	0.2362	3.34566	17.21
27.5015	599.78	0.2362	3.24333	7.00
28.6919	1793.44	0.2362	3.11143	20.92
29.4340	8572.72	0.2362	3.03465	100.00
30.0691	1568.87	0.2362	2.97199	18.30
30.8043	1444.61	0.2362	2.90271	16.85
32.2330	3745.17	0.2362	2.77724	43.69
32.6300	3055.78	0.1574	2.74435	35.65
34.0857	8546.21	0.2362	2.63040	99.69
34.9519	1210.81	0.2362	2.56718	14.12
36.0092	892.96	0.2362	2.49419	10.42
36.6670	582.20	0.2362	2.45094	6.79
37.2757	545.88	0.2362	2.41230	6.37
38.8375	688.11	0.2362	2.31882	8.03
39.4565	1399.72	0.2362	2.28386	16.33
40.8349	1344.38	0.2362	2.20989	15.68
41.2989	2360.04	0.2362	2.18613	27.53
41.8453	1165.98	0.2362	2.15884	13.60
43.2159	1914.70	0.3149	2.09350	22.33

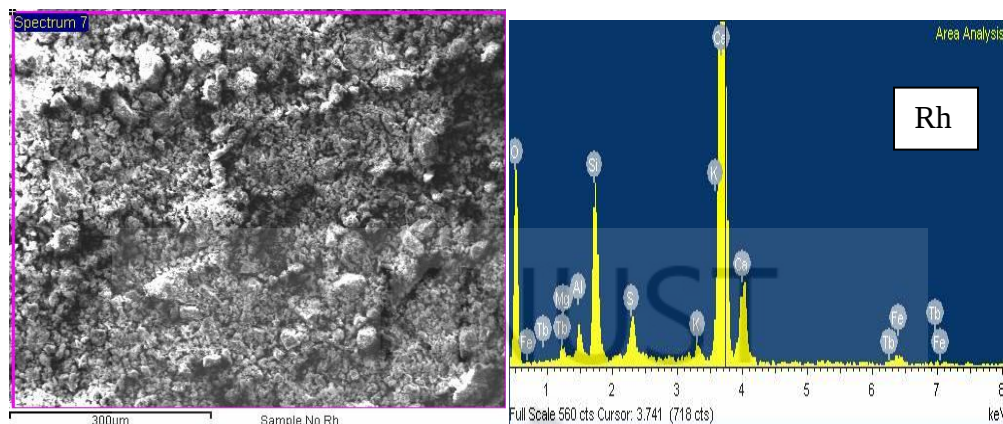
44.0350	1573.09	0.4723	2.05644	18.35
44.7352	1420.03	0.2362	2.02586	16.56
45.8004	1611.76	0.2362	1.98119	18.80
47.1176	5241.64	0.3149	1.92884	61.14
48.5536	1607.49	0.3149	1.87510	18.75
50.0281	1482.48	0.4723	1.82323	17.29
50.8042	3162.35	0.2362	1.79719	36.89
51.7810	2333.25	0.2362	1.76556	27.22
53.2112	443.17	0.4723	1.72143	5.17
54.3503	1591.06	0.2362	1.68802	18.56
55.1541	546.52	0.2362	1.66530	6.38
56.5570	1187.78	0.3149	1.62728	13.86
57.4536	696.42	0.2362	1.60400	8.12
58.6461	666.80	0.3149	1.57420	7.78
59.4382	515.20	0.1574	1.55510	6.01
60.0261	1271.48	0.2362	1.54127	14.83
60.7303	744.12	0.2362	1.52507	8.68
62.4985	1803.53	0.4723	1.48611	21.04
63.6700	530.70	0.1574	1.46156	6.19
64.2233	1132.60	0.3149	1.45030	13.21
65.7647	296.45	0.3936	1.41999	3.46
67.3986	214.71	0.3936	1.38949	2.50
68.2895	268.13	0.3149	1.37352	3.13
70.4317	246.88	0.3936	1.33690	2.88
71.7591	839.01	0.3149	1.31541	9.79
73.0035	203.51	0.2362	1.29603	2.37
77.6842	237.82	0.3149	1.22922	2.77
79.2222	367.57	0.2362	1.20917	4.29
80.2300	242.06	0.3149	1.19651	2.82
81.7974	445.32	0.3149	1.17750	5.19
83.1602	330.34	0.3936	1.16163	3.85
83.8371	503.10	0.3840	1.15302	5.87



Resolved XRD graph of 5%Limestone cement used to calculate % composition

APPENDIX III

SEM/EDX graphs and computer generated values



Spectrum processing : No peaks omitted

Processing option : All elements analyzed (Normalised)

Number of iterations = 5

Standard :

C CaCO₃ 1-Jun-1999 12:00 AM

O SiO₂ 1-Jun-1999 12:00 AM

Mg MgO 1-Jun-1999 12:00 AM

Al Al₂O₃ 1-Jun-1999 12:00 AM

Si SiO₂ 1-Jun-1999 12:00 AM

S FeS₂ 1-Jun-1999 12:00 AM

K MAD-10 Feldspar 1-Jun-1999 12:00 AM

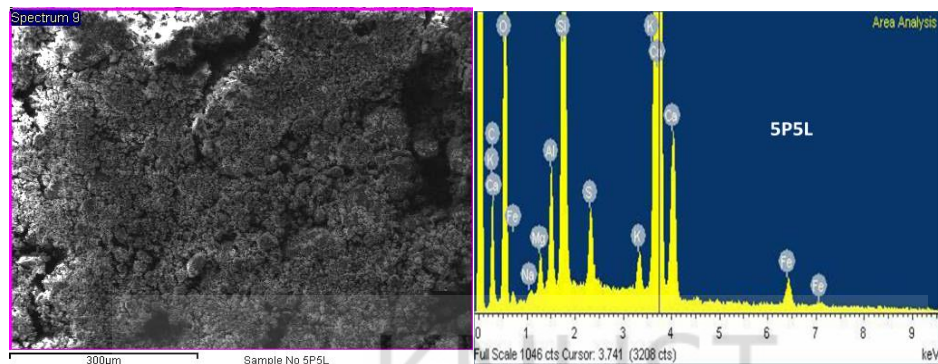
Ca Wollastonite 1-Jun-1999 12:00 AM

Fe Fe 1-Jun-1999 12:00 AM

Tb TbF₃ 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%	
C K	8.67	14.79	
O K	48.21	61.77	
Mg K	0.24	0.20	
Al K	1.06	0.81	
Si K	5.52	4.03	
S K	1.39	0.89	
K K	0.70	0.37	
Ca K	32.63	16.69	
Fe K	1.07	0.39	
Tb L	0.51	0.07	
Totals	100.00		

Sample 5P5L



Spectrum processing : No peaks omitted

Processing option : All elements analyzed (Normalised)

Number of iterations = 5

Standard :

C CaCO₃ 1-Jun-1999 12:00 AM

O SiO₂ 1-Jun-1999 12:00 AM

Na Albite 1-Jun-1999 12:00 AM

Mg MgO 1-Jun-1999 12:00 AM

Al Al₂O₃ 1-Jun-1999 12:00 AM

Si SiO₂ 1-Jun-1999 12:00 AM

S FeS₂ 1-Jun-1999 12:00 AM

K MAD-10 Feldspar 1-Jun-1999 12:00 AM

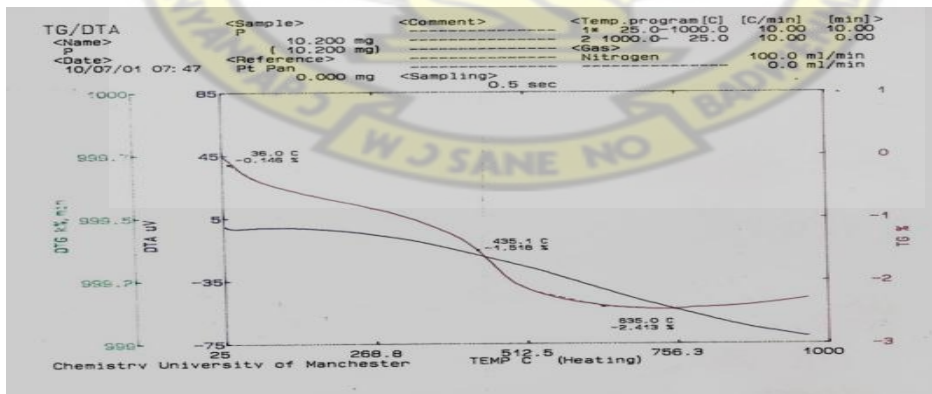
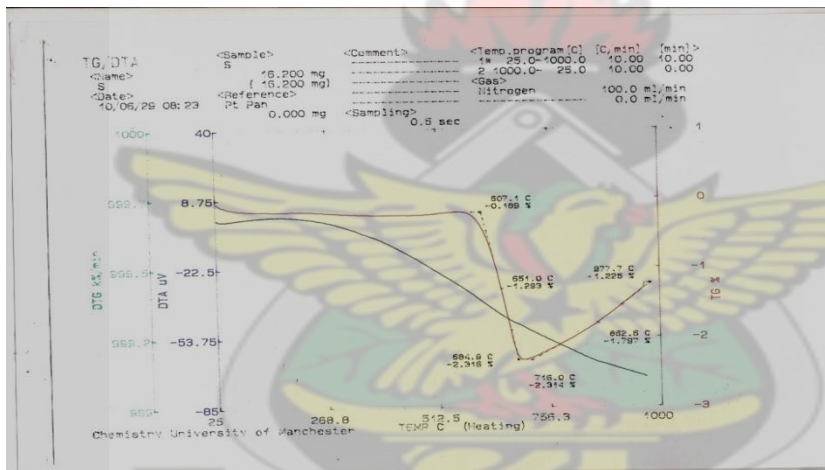
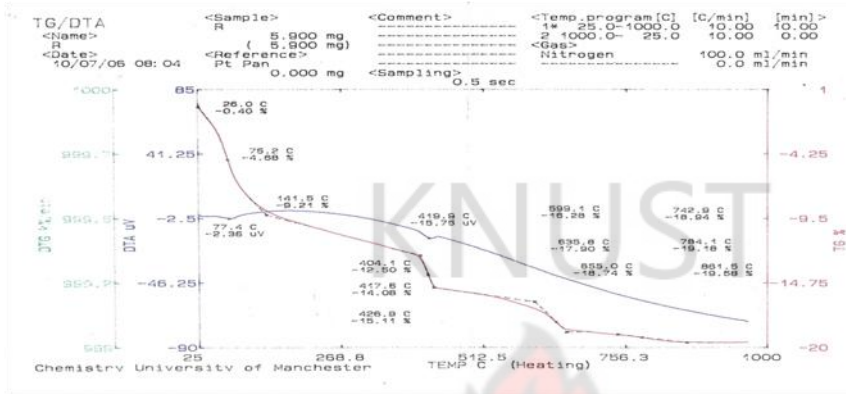
Ca Wollastonite 1-Jun-1999 12:00 AM

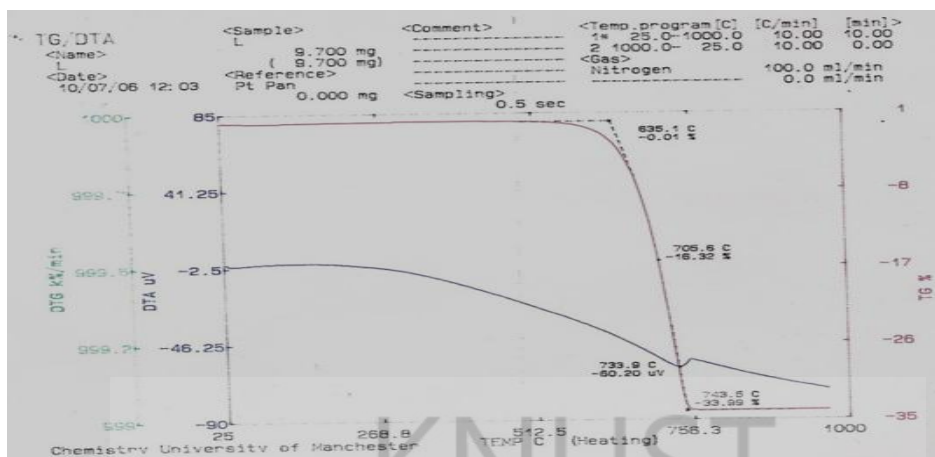
Fe Fe 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	9.80	16.12
O K	50.57	62.43
Na K	0.15	0.12
Mg K	0.62	0.50
Al K	1.55	1.13
Si K	6.45	4.54
S K	1.15	0.71
K K	0.70	0.35
Ca K	27.52	13.56
Fe K	1.50	0.53
Totals	100.00	

APPENDIX IV

TG/DTA THERMOGRAPHS OF BLENDED CEMENTS





KNUST

