UTILIZATION OF SOME GHANAIAN MINERAL ADMIXTURES FOR MASONRY MORTAR FORMULATION

BY

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by

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DECLARATION

I hereby declare that this submission is my own work towards the MPhil and that, to the best of my knowledge, it contains no material 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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Head of Dept. Signature Date

DEDICATION

THIS WORK IS DEDICATED TO MY DEPARTED SISTER, FLORA BEDIAKO. MAY HER SOUL REST IN PERFECT PEACE.

ABSTRACT

The suitability of masonry mortar for various constructional applications is dependent on some vital engineering properties and production cost. In majority of masonry formulations, ordinary Portland cement (OPC) is the principal binding agent. However, the current trend of cement cost in Ghana has rendered masonry mortar formulation quite expensive. Meanwhile in other parts of the world, different types of admixtures which are either chemical or mineral products are well known to improve mechanical and economical values of formulated mortars. In this study, two available mineral admixtures namely clay pozzolana (CP) and limestone (L) were used as partial replacement of OPC at 10%, 20%, 25%, 30%, 35% and 40% to formulate binary paste and mortar whilst 10%CP and 20%L, 20%CP and 10%L, 15%CP and 15%L, 30%CP and 20%L batch mixes were prepared for the ternary paste and mortar mixes. Mankranso clay and Orterkpolu limestone deposits were used. Physical, chemical, mineralogical and microstructure analysis were carried out on the mineral admixtures. Mechanical properties such as water demand, setting times, compressive strength and aspects of durability studies were determined. The economic analysis of utilizing the mineral admixture in masonry mortar over plain mortar was studied. Test results indicated that CP and L that were utilized were of standard quality in accordance to ASTM and EN 197-1 standard specifications. Formulated binary and ternary paste and mortar showed appreciable mechanical properties. In accordance to ASTM C270, OPC replacement by 25%CP and 30%L produced a type M mortar whereas 35%L and 40%CP produced a type S mortar. Economically, formulated type M mortar could make savings between 12.5%- 15% whilst type S mortar could make 17.2%- 19.9% over a plain cement mortar.

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CHAPTER ONE

1.1 INTRODUCTION

In the world today, mineral admixture utilization as cementitious materials to replace part of ordinary Portland cement (OPC) in the field of mortar and concrete production has found extensive applications (Tontanji and Bayasi, 1999). Mineral admixtures are known to be cementitious powders and the most common ones usually blended with Portland cement are latent hydraulic components like blast furnace and steel-making slag, pozzolanic materials like pozzolana, fly ash, rice husk ash, condensed silica and burnt clay or filler component like limestone, clamshells and other waste materials (Hernandez *et al*, 1998 and Mehta, 1994).

Many authors have reported that the reason for utilizing mineral admixtures is diverse. Targan *et al* (2002) reported that mineral additions to Portland cement have been an interesting subject of research for economical, environmental and technical reasons. Toledo Filho *et al* (2007) reported that in the year 2000, the world's emission of carbon dioxide from fossil combustion and industrial processes was 25 billion tonnes out of which cement production contributed 5%. On the technical advantages of mineral admixtures utilization, several authors have reported that they improve strength (Caldarone *et al*, 1994), workability (Wild *et al*, 1996), durability (Xin Li *et al*, 2006) and also reduce thermal hydration of mortar and concrete (Coleman & Page, 1997).

The utilization of mineral admixtures has led to the formulation of binary, ternary and even quaternary blends. The current European standard on cement EN 197-1 has standardized binary blends. These are Portland composite type II/A-M comprising 6-20% mineral additions and type II/B-M comprising 21-35% mineral addition. Ternary and quaternary blends are now produced commercially in France and Australia (Berry, 1980). In Canada silica fume and fly ash are used in ternary mixture production at St Constant in Quebec. The formulation of masonry cement for masonry mortar could be produced from a binary, ternary or a quaternary mixture.

1.2 Statement of problem

The production of masonry mortar from Portland cement (PC) and the utilization of blended cements for masonry works have been found to be associated with diverse problems.

Firstly, the high cost of ordinary Portland cement in the country has led to a high cost of masonry mortar formulation. This is because cement clinker used to manufacture Portland cement has always been imported from Europe and other parts of Asia. The trend of Portland cement prices for the past 8 years has been found ever increasing annually. It is also found that between the years 2000 and 2008 the percentage price increase has been about 270%. The price per bag of Portland cement is expected to continue to increase due to the overdependence of the country on clinker importation. In 2007 clinker consumption was 3.5 million tonnes and is expected to hit about 5.5 million tonnes by 2010 (Anon, 2007).

Secondly, the use of ordinary Portland cement for masonry works like plastering, rendering and jointing is reported by Sandin (1995) to be harsh and hard. The harsh nature in cement hydration mostly results in the creation of hairline cracks in mortar renders on walls after Portland cement has set (Neville, 1994). Rain water is drawn by capillary action into these cracks and then diffuses into the wall. Once inside the wall this moisture, together with any rising dampness and water vapour generated by life, is trapped, as it cannot evaporate through the hard impermeable render. The moisture level starts to build up in the wall and the moisture shows on the inner surface of the wall, resulting in internal dampness and damage to plasters and decoration (Anon, 2006). Blended cements could be a better remedy to control the harsh nature of Portland cement during hydration.

Thirdly, the technology of using mineral admixtures in conjunction with Portland cement is unfamiliar as blended cement mortars is very unfamiliar to most builders and engineers in Ghana. Builders and construction engineers carry diverse perceptions on mineral admixture utilization. Some of these perceptions are mortar strength reduction, unpredictable workability, crack formation, less durable mortars etc.

Finally, there also exists little information on mortar class specifications involving blended mixtures. Most developed countries in the world have mortar class specification data. A typical example could be found in the America Standard for the testing of materials, ASTM C 270.

1.3 Objectives

The objectives of the research were as follows:

- Formulate binary and ternary masonry paste and mortar using calcined clay pozzolana and limestone powder in varying proportions.

- Analyse the suitability of binary and ternary paste and mortar formulations using Mankranso clay pozzolana and Orterkpolu limestone.
- Compare the cost of plain mortar formulation and the blended mortar formulations

1.4 Justification

The following reasons constituted the justifications for the research:

- Mineral admixtures which are readily available in Ghana but not commonly used could provide alternative mortar for masonry works
- The production and processing of mineral admixture as a cementitious material is less expensive than Portland cement processing. The reason is that, less mechanized equipment and less energy are required for mineral admixture processing into cementitious materials whilst Portland cement production requires mechanized equipment and more energy (Davraz and Gunduz, 2005). This indicates that less expensive cementitious material could be used to replace part of more expensive ordinary Portland cement.

1.5 Scope of work

The study focused attention on analyzing the physical, chemical, mineralogical and microstructural properties of calcined clay pozzolana and limestone powders.

It investigated some mechanical properties that included compressive strength, water demand, setting times and an aspect of durability studies. The aspect of durability studies focused attention on the resistance of the blended mortars against sulphate solution which will be compared with the blended mortars cured in water.

Finally the study also looked at the economic analysis of both plain and blended mortars.

CHAPTER TWO

2.1 LITERATURE REVIEW

2.2 Definition of Masonry Cement

According to BS.5224:1976, masonry cement consists essentially of Portland cement (normally more than 75%) with an air entraining agent and a proportion of other materials to improve plasticity, water retention and frost resistance. The other materials may or may not be hydraulically inert. An example of hydraulically active material is slag. Hydraulically inert materials include limestone, natural or artificial pozzolana, fine silica etc.

ASTM C91 also defines masonry cement as a hydraulic cement for use in mortars for masonry construction, containing one or more of the following materials: ordinary Portland cement, Portland-pozzolana cements, natural cement, slag cement, or hydraulic lime and in addition usually containing one or more materials such as hydrated lime, limestone, chalk, calcareous shell, talc, slag or clay as prepared for this purpose. The constituents for masonry cement may vary depending on the manufacturer, local construction practices and climatic conditions (Anon, 2003).

Considering the two definitions, the BS standards emphasize on air entraining agents whilst the ASTM standards does not. Masonry cement components are mostly proportioned at the plant under controlled conditions to ensure uniformity or performance. They can also be produced by the mixing technology during the mortar or concrete mixing or batching process.

It has been known for many years that mineral admixtures, chemically inert or not, modify the physical and mechanical properties of concrete when they are used as cementitious material (Lawrence *et al*, 2003).

2.3 Types of Masonry Cement

Masonry cement is normally used for masonry mortar production. In building construction a variety of mortars prepared from different binders have been used for plastering and jointing purposes. Examples of these are lime, cement and composite mortars (Malhotra and Dave, 1999). The ASTM C91 classifies masonry cement into three types namely type M, S and N. These arbitrary designations were assigned by taking every other letter from the term "mason". Mortars are differentiated primarily by their strength. M is the highest strength, S is the next and N is a moderate strength mortar (Portland cement association, 2002).

Masonry cement mortar is used for specific applications of building segments. Table 2.1 gives recommended guide for mortar type selection.

Table 2.1 Recommended Guide for selection of mortar type

Building Segment	Type
Exterior above grade	
load- bearing	N or S
non- load bearing	N
Exterior at or below grade	S or M
Interior	
load- bearing	N or S
non- load bearing	N

(Source: Portland cement Association, 2002)

ASTM C 1157 standard has introduced performance-based hydraulic cements that do not limit the type and the amount of mineral additions that can be blended with Portland cement.

In Europe, the standards for Portland cement composite cements, EN 197-1 identifies two types of active mineral additions. These are type II/A-M containing 6–20% and type II/B-M containing 21–35% of mineral additions. These cements, as other types defined by this standard, can contain a proportion of up to 5% of minor examples of such constituents. These cements are classified for different strength classes according to the strength gain after 28 days of curing (Carrasco *et al.*, 2005).

2.4 Portland cement

Cement is defined as a powdered material that chemically reacts with water and therefore attains the property of setting and hardening (Neville, 2002). This property makes cement hydraulic. Ordinary Portland cement is produced by intimately mixing together clay and limestone and then burning the mixture at high temperature (1300-1450°C) to form clinker. The clinker is then ground together with a small amount of gypsum into powder (Akroyd, 1962). Table 2.2 shows the chemical composition of ordinary Portland cement.

Table 2.2 Chemical composition of Portland cement

Composition	Range (%)	Average
Lime(CaO)	59 to 67	64
Silica (SiO_2)	17 to 25	21
Alumina(Al_2O_3)	3 to 9	7
Iron Oxide(Fe_2O_3)	0.5 to 6	3
Magnesia (MgO)	0.1 to 4	2
Sodium Oxide (NaO)	0.5 to1.3	2
Potassium Oxide (K_2O)	0.5 to 1.3	1.2
Sulphur trioxide ($S0_3$)	1 to 3	2

Source: Akroyd, 1962

The chemical compositions are combined in various forms during calcinations to form cement compounds. Four major compounds that constitute ordinary Portland cement compounds are shown in Table 2.3.

Table 2.3: Main compounds of Portland cement

Name of compound	Oxide composition	Abbreviation
Tricalcium silicate	$3CaO.SiO_2$	C_3S
Dicalcium silicate	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$3CaO.Al_2O_3$	C_2A
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF

Source: Neville, 1996

The tricalcium silicate (C_3S) and the dicalcium silicate (C_2S) together form 70-80% of Portland cement. C_3S and C_2S control its characteristics. A high percentage of C_3S

and a corresponding low amount of C_2S will give a high early strength and generate a considerable heat in the hydration process. A reverse combination results in a slower development of strength and generation of less heat.

The tricalcium aluminate (C_3A) content is the least desirable cement compound but very important. It hydrates rapidly and generates more heat during hydration. It has been found that cement with low percentage of C_3A will develop a high ultimate strength with less heat of hydration, will show greater volumetric stability, less tendency to cracking and more resistant to acid and sulphate attack, than a cement with a high C_3A (Akroyd, 1962).

In the chemical composition of Portland cement, lime (CaO) is mostly derived from the decomposition of calcium carbonate ($CaCO_3$). It has been realized that high lime content (more than 67%) gives a slow setting product with a high early strength but an excess may cause unsoundness of cement.

Silicon dioxide (SiO_2) is derived from clay or shale used as raw material for cement processing. Pure crystalline silica occurs in nature as quartz. Quartz is a very inert substance chemically at ordinary temperature, but when strongly heated it reacts vigorously with bases. Quartz will react with lime in the presence of water, if heated under pressure.

Aluminium oxide (Al_2O_3) and Ferric oxide (Fe_2O_3) contents in a cement need to be considered together, since although they are by no means equivalent to one another, their effects are closely interconnected (Lea, 1970). They form the compounds C_3A

and C_4AF; the relative proportion of these two compounds depends on the ratio of alumina to ferric oxide present. Increase with alumina with no change, or with a reduction, in the ferric oxide content, hastens the setting of a cement and a point is eventually reached at which it becomes impossible to control the setting time adequately.

Magnesia (MgO) is only present in small quantities in Portland cement and is derived from magnesium carbonate present in original limestone in the form of dolomite, $CaCO_3.MgCO_3$, or to a small extent from clay or shale. Increased presence of MgO (greater than 2%) may be detrimental to the soundness of cement, especially at late ages. Beyond that limit it appears in clinker as free MgO called periclase. Periclase reacts with water to form Mg $(OH)_2$, and this is the slowest reaction among all other hardening reactions. Since $Mg(OH)_2$ occupies a larger volume than the MgO and is formed on the same spot where the periclase particle is located, it can split apart the binding of the hardened cement paste, resulting in expansion cracks commonly known as magnesia expansion (Ali *et al*, 2008)

Sulphur trioxide (SO_3) present in cement is derived principally from gypsum ($CaSO_4$) added to clinker before grinding. To control setting times effectively, Portland cement needs a minimum amount of gypsum which is added to the clinker. High percentage of SO_3 (above 2.5%) tends to cause unsoundness of cement.

Loss of ignition (LOI) is at times presented as a chemical constituent of Portland cement. A high LOI indicates prehydration or carbonation, which may be caused by improper and prolonged storage or adulteration of cement during transport or transfer. The minimum LOI specified by most standard specification for Portland cement is 4% (Ali *et al*, 2008).

2.5. Cementitious mineral materials

A given cementitious material may be hydraulic in nature, that is, it may undergo hydration on its own in the presence of water and contribute to the strength of concrete and mortar. Alternatively, it may have latent hydraulic properties: that is, it may exhibit hydraulic properties only in the consequence of chemical reaction with some other compounds such as the products of hydration of Portland cement, which coexists in the mixture. The third possibility is for the material to be largely chemically inert but to have a catalytic effect on the hydration of other materials; such materials are normally called fillers. Cementitious materials have one common property and that is they are at least as fine as the particles of Portland cement (Neville, 1996). Table 2.4 describes the relevant properties of some cementitious materials.

Table 2.4: Cementitious nature of materials in blended cement

Material	Cementitious nature
Portland cement clinker	Fully cementitious (hydraulic)
Ground granulated blastfurnace slag	Latent hydraulic, sometimes hydraulic
Natural pozzolan	Latent hydraulic with Portland cement
Siliceous fly ash	Latent hydraulic with Portland cement
High- lime fly ash	Latent hydraulic with Portland cement- but also slightly hydraulic
Silica fume	Latent hydraulic with Portland cement- but largely physical inaction
Calcareous filler	Physical in action but with slight latent hydraulic action with Portland cement .
Other fillers	Chemically inert; only physical in action

(Source: Neville, 1996)

The advent of cementitious materials has made it possible to utilize large portions of these minerals in binary, ternary, and even quaternary component blended cements.

2.6 Binary blends

Menendez *et al* (2003) stated that, around the world binary blended cements are standardized. Some of these binary blended cements are Portland slag cement, pozzolanic cements and limestone filler Portland cements. Pozzolanic cement was standardized in Italy in the year 1929, blast-furnance slag cements were produced in Germany, France, Luxembourg and Belgium between the seventeenth and eighteenth century, and cements containing fly ash appeared in France in 1950 (Carrasco *et al*, 2005).

The combination of a cementitious material and Portland cement can be termed as binary blend. Many researchers have found that binary blended cements produce better quality and durable mortar and concrete than plain Portland cement (Gruber *et al*, 2003; Dunster *et al*, 1993; Cabrera and Nwanbani, 1993). The literature presents some common minerals used as cementitious materials in the formulation of binary blended cements. Knowledge of binary blended cement will be an advantage in understanding the principle of ternary blended cement formulation.

2.6.1 Pozzolana

Pozzolana is defined as a siliceous or alumino-siliceous material, which in itself possesses little cementitious value, but in finely divided form and in the presence of water chemically reacts with free lime from cement at ordinary temperature to form compounds possessing cementitious properties (Swamy, 1990 and Lea, 1970). Pozzolana occurs naturally and artificially. Examples of natural pozzolanas are volcanic glasses and ashes, tuff, trass and Santorin earth all found in the US and some parts of Europe.

Rhenish trass is obtained from quarries consisting of an isotropic ground containing various crystalline mineral constituents such as feldspar, leucite and quartz with small amounts of augite, hornblend, mica etc. Trasses can also be found in Rumania and former USSR.

Santorin earth consists mainly of a granular isotropic material mixed with pumice, obsidian and fragments of crystalline feldspars, pyroxenes, quartz etc. The Italian pozzolanas occur in the neighbourhood of Vesuvius and around Naples as incoherent trachytic tuffs, and around Rome (Lea, 1970).

The volcanic materials owe their pozzolanic properties both to the volcanic glass and to the altered zeolitic compounds (Malquiro, 1960). The zeolite found includes herchillite, phillipsite, chabazite and analcite. These are compounds of the type $(R_2Ca)O.Al_2O_3.4SiO_2.XH_2O$ that differ in the contents of calcium and alkali cations. Analcite approximates to $Na_2.Al_2O_3.4SiO_2\ 2H_2O$, chabizite to $(R_2Ca)O.Al_2O_3.4SiO_2.6H_2O$ rich in lime, herschellite $(Ca,Na)(Al_2SiO_{12}).6H_2O$ to a corresponding compounds richer in alkalies and philipsite $(K)(Al_2S_{14})O_{12}.4.5H_2O$ to a potash-rich compound (Lea, 1970). Artificial pozzolanas include flyash, burnt gaize, moler, calcined clays and shales, industrial by-products such as silica fume and granulated slag, rice husk ash.

Fly ash produced from coal combustion is the most widely used pozzolanic material in the world. ASTM C618 gives the different classifications of fly ash, based on the type of coal from which the ash originates. The most common fly ash derived from bituminous coal is mainly siliceous and is known as Class F fly ash. Sub-bituminous coal and lignite result in high lime ash, known as Class C fly ash (Neville, 1996).

Gaize is a soft, porous, highly siliceous, sedimentary rock containing a proportion of clay. It is commonly found in the Meuse valley in France.

Calcined clay pozzolanas are produced by burning suitable clays at a temperature which varies from 600°C to over 900°C depending on the nature of clay. Read and Rutley (1970) have identified and explained many categories of clays, however, Lea

(1970) indicates kaolinite, montmorillonite, hydromicas and illite groups as the most commonly utilized clay type for pozzolana production.

Singh and Garg (2006) reported that the use of calcined kaolinitic clay as a pozzolanic material is not very popular. Calcined kaolinitic clay also known as metakaolin is processed from high-purity kaolin clay by calcination at moderate temperatures (650-850°C). Ambroise *et al* (1985) showed that calcinations below this temperature result in less reactive metakaolinite with more residual kaolinite. Above 850°C crystallization occurs and reactivity declines (Lea, 1938). If clays are heated at higher calcining temperatures, liquid phase forms solidify on cooling into an amorphous glass phase. Amorphous glass also shows pozzolanic activity as in the case of fly ash (FAs), which is normally composed of 70-90% glass phase.

In Ghana, the Building and Road Research Institute (B.R.R.I) of the Council for Scientific and Industrial Research (C.S.I.R) has extensively researched into some local materials which can be used for artificial pozzolana production. In the studies of Hammond (1976 and 1978), he mentioned that bauxite waste could be a very good pozzolanic material when calcined at a temperature between 700°C and 900°C. Moreover, some research efforts from Atiemo (1994) and Momade & Atiemo (2004) showed that clay could be calcined at 600- 1000°C to produce reactive pozzolana. Examples of the clay deposits they studied were Hwereso and Asokwa in Ashanti Region, Nkosia and Mankessim in the Central Region.

2.6.2 Chemical composition of natural pozzolana

The chemical properties of natural pozzolana vary depending on the region of the source (Malhotra, 1987). Natural pozzolanas are mostly of volcanic origins and are composed of silicates and other glass and crystalline particles. They are obtained from open pits and quarries. Table 2.5 indicates the chemical composition of some volcanic ash pozzolanas obtained from different pits and quarries in the world.

Table 2.5: Percentage composition of volcanic ash pozzolanas

Pozzolana	Ignition Loss	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3
Rhenish Trass	10.1	54.6	16.4	3.8	0.6	3.8	1.9	5.1	3.9	0.4
Rhenish Trass	8.5	54.8	17.2	4.4	0.6	2.3	0.9	7	3.8	0.1
Bavarian Trass	14.5	57	10.9	5.6	0.5	6	2.2	1.8	1.5	0.2
Santorin Earth	4.9	63.2	13.2	4.9	1	4	2.1	3.9	2.6	0.7
Santorin Earth	3.1	65.2	12.9	6.3	—	3.2	1.9	2.6	4.2	—
Rome:Segni	9.6	44.1	17.3	10.7	—	12	2	1.4	3.1	—
Segni	5.3	48.2	21.9	9.6	—	7.5	3.2	4.1	4.1	0.3
S.Paolo	4.1	45.2	20	10.7	—	9.8	3.8	6.2	6.2	0.3
Naples:Bacoli	4.8	55.7	19	4.6	—	5	1.3	11.3	3.9	
Baia	4.4	59.5	19.3	3.3	—	2.1	0.2	2.9	11.3	0.2
Rumania Trass	13.9	62.5	11.6	1.8	—	6.6	0.7	3.7	2.9	—
Crimean Tuff	11.7	70.1	10.7	1	—	2.5	0.3	5	3.7	—
Rhyolltic	3.4	65.7	15.9	2.5	—	3.4	1.3	1.6	1.9	—
Pumicite	4.2	72.3	13.3	1.4	—	0.7	0.4	4.2	5.4	Trace

(Source: Lea, 1970)

2.6.3 Chemical composition of artificial pozzolana

The chemical composition of some artificial pozzolanas is shown in Table 2.6. The major chemical component is normally silicates with other minor chemical components.

Table 2.6: Percentage composition of some artificial pozzolanas

Pozzolana	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O and K_2O	SO_3	Ignition Loss
Burnt clay	60.2	17.7	7.6	2.7	3.9	4.2	2.5	1.3
Spent oil shale	51.7	22.4	11.2	4.3	2.5	3.6	2.1	3.2
Raw gaize	79.6	7.1	3.2	2.4	1.1	—	0.9	5.9
Burnt gaize	88.0	6.4	3.3	1.2	1.0	—	Trace	—
Raw Moler	66.7	11.4	7.8	2.2	0.8	—	1.4	5.6
Burnt Moler	70.7	12.1	8.2	2.3	2.1	—	1.5	—
Raw diatomite (USA)	86.0	2.3	1.8	Trace	0.6	0.4	—	8.3
Fly-ash (USA)	47.1	18.2	19.2	7	2.2	3.95	2.8	1.2
Fly-ash (British)	45.9	24.4	12.3	3.6	2.5	4.2	0.9	4.1

(Source: Lea, 1970)

2.6.4 Mineralogical composition of pozzolanic materials

The mineralogy of a pozzolanic material varies; depending on the particular type of pozzolana it originates from i.e. as to whether it is natural (e.g. trasses, tuffs etc) or artificial (e.g. fly ash~~es, silica~~ fume, calcined clays and shales, etc).

On the mineralogy of natural pozzolana, the work of Ghrici *et al* (2007) showed an example indicating the presence of quartz, corderite, hematite, analcine and axinite represented in figure 2.1.

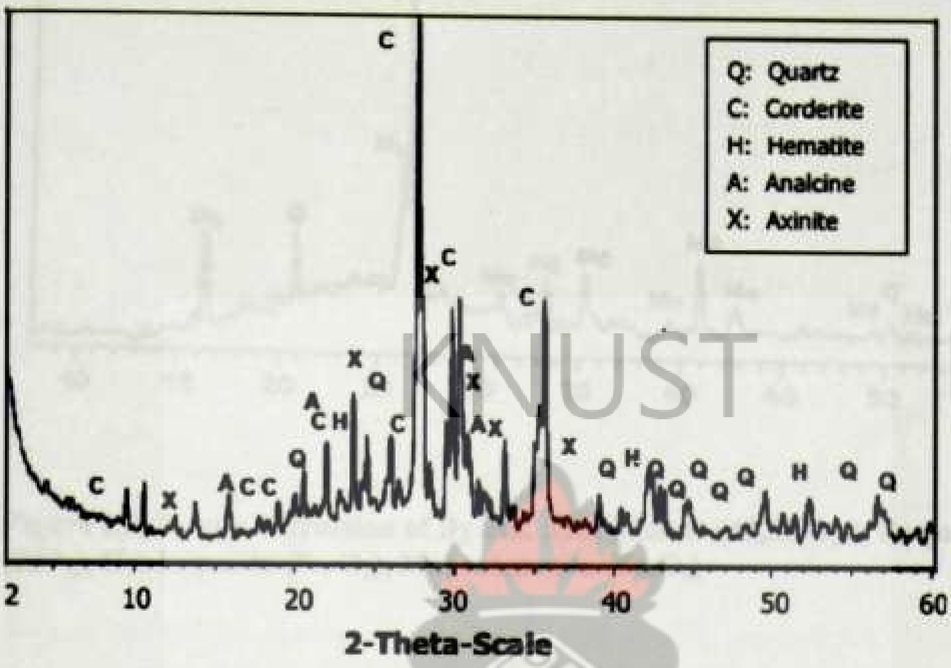

Figure 2.1: X-ray diffraction of natural pozzolana

The mineral composition of fly ash pozzolana is divided into four groups, namely, glass phase which is responsible for pozzolanic activity, crystalline phase which is mostly mullite with composition ranging from quartz, hematite (Fe_2O_3), magnetite (Fe_3O_4), diopside (Ca, Mg).Si_2O_6), wollastonite ($CaO.SiO_2$) and minor residues of incompletely transformed clay minerals. The last is secondary constituents which are composed of unburnt coal, free lime (CaO), periclase (MgO) and soluble metal salts. Figure 2.2 represents an example of a diffractogram pattern which was illustrated by Elkhadiri *et al* (2002).

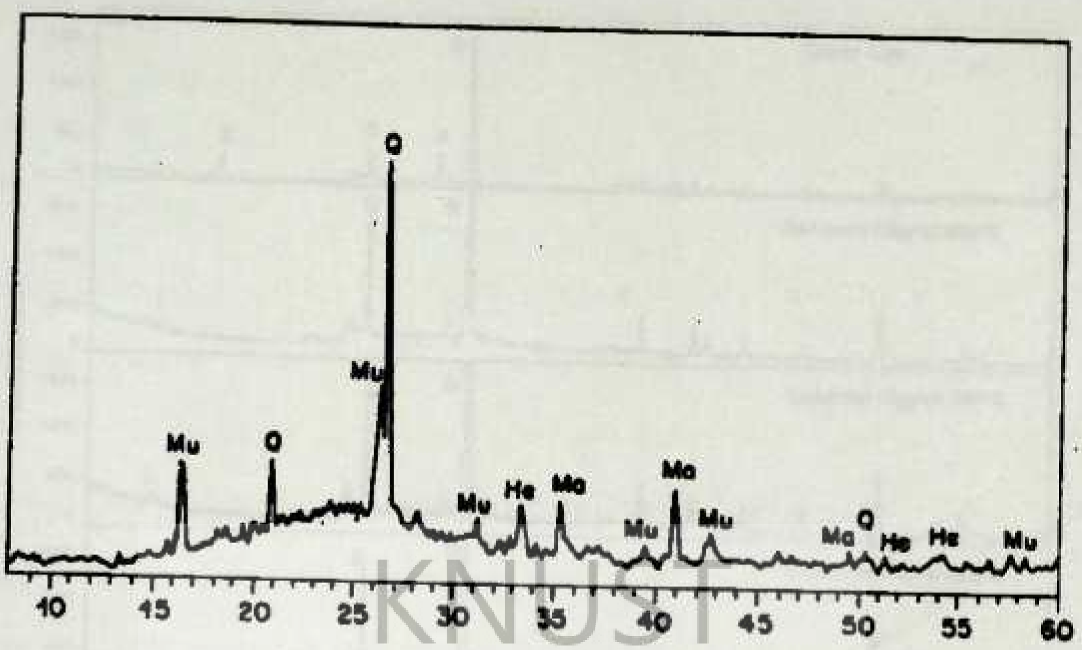

Figure 2.2: X- ray diffraction of fly ash. **Mu:** Mullite ($Al_6Si_2O_{13}$), **Q:** quartz (SiO_2), **He:** hematite (Fe_2O_3), **Ma:** magnetite (Fe_3O_4)

The mineral composition of calcined clay pozzolana as well as crude clay has been investigated by Chakchouk *et al* (2006) and the X-ray analysis is shown in figure 2.3. The figure indicate that the peaks corresponding to kaolinite, initially present in the crude clay, disappeared in all the heated clay samples patterns at 600, 700 and 800°C. They stated that the presence of a dome between 20 and 30° confirms the transformation of the kaolinite to an amorphous phase. Chakchouk *et al* (2006) also concluded that as the diffractograms of the calcined clay samples were similar at 600, 700 and 800°C, it therefore implied that the temperature of 600°C was sufficient to produce clay pozzolana.

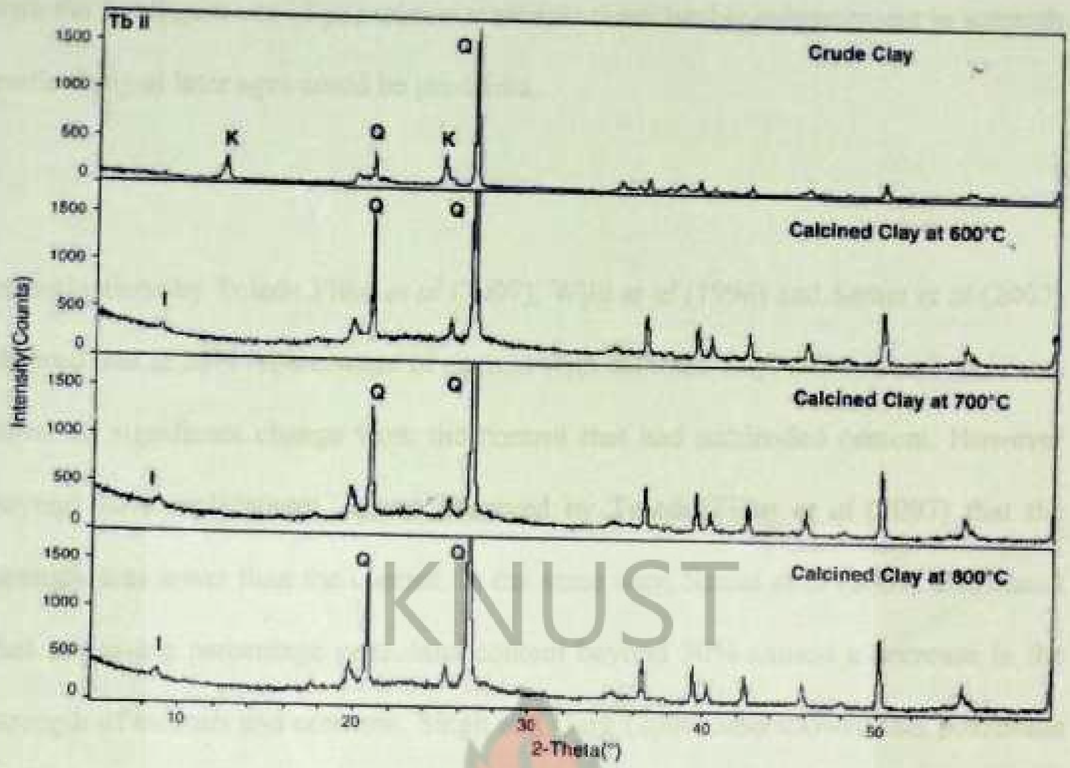

Figure 2.3: XRD patterns of heat treated clay at 600, 700 and 800°C and untreated clay sample. K: kaolinite, I: illite, Q: quartz

2.6.5 Mechanical properties of Pozzolanic cement mixtures

The mechanical properties considered under this discussion include the following:

1. Compressive strength of blended pozzolana mortar
2. Water demand of blended pozzolana paste and
3. Setting times of the blended pozzolana paste

2.6.5.1 Compressive strength of blended pozzolana mortar

Several studies have ~~shown the~~ strength characteristics of mortar and concretes containing both natural and artificial pozzolanas. The studies have also shown that with the intelligent use of pozzolanic materials considerable enhancement in strength particularly at later ages could be produced.

Investigations by Toledo Filho *et al* (2007), Wild *et al* (1996) and Samet *et al* (2007) showed that at 20% replacement of cement with calcined clay, mortars and concretes show no significant change from the control that had unblended cement. However beyond 30% replacement, it was observed by Toledo Filho *et al* (2007) that the strength was lower than the control. In the same way, Samet *et al* (2007) also found that increasing percentage pozzolana content beyond 30% caused a decrease in the strength of mortars and concrete. Singh and Garg (2006) also showed that pozzolana content ranging from 10-25% in ordinary Portland cement is recommended for all types of construction. This observation is similar to Shannang and Yeginobali's (1995) who showed the optimum mix for natural pozzolana to be 25%. Peckmeszci and Akyuz (2004) reported that pozzolana has a negative effect on the compressive strength when used in high content.

A recent investigation by Ezziane *et al* (2007) on the compressive strength of mortar containing natural pozzolana available in Algeria is shown in Table 2.7. The table shows that the strength of the mortar increases with curing time from 1 to 90 days. Mortar containing 20% pozzolana content showed the maximum values being 33.3MPa and 40.2MPa at 28 and 90 days respectively. From table 2.7, above 20% and up to 40% pozzolana content, the strength values with respect to curing days at 1, 2, 7, 28 and 90 days were seen decreasing.

Table 2.7: Compressive strength results of mortar at 20°C

% Replacement level	Compressive strength (MPa)				
Pozzolana	1d	2d	7d	28d	90d
0	7.7	15.2	22.4	30.3	34
10	6.7	15.5	21.2	33.1	39.6
20	5.6	21.2	19.8	33.3	40.2
30	4.8	33.1	16.5	30.7	33.8
40	3.5	6.8	14.4	26.1	30.3

Source: Ezziane *et al*, 2007

Fly ash which has already been reported as the commonest pozzolanic material in the world has also been extensively used for major concretes and dams construction in USA, Europe and Asia. In Thailand, Chindaprasirt *et al* (2005) investigated the use of class F fly ash as a partial replacement of ordinary Portland cement at a percentage of 20 and 40 of mixed cement for jointing and plastering respectively. They found that adequate strength development was found in mortars containing 20-40% fly ash as cement replacement for type N and S mortars.

Pozzolana from bauxite has been investigated by Nwoko and Hammond (1979). They found that concrete containing bauxite pozzolana content up to 40% produced strength values of between 22.1MPa and 33.0MPa at 28 days of water curing which was within the acceptable compressive strength value of 24MPa as require by the ASTM standard.

In the studies of Atiemo (1994), he stated that Hwereso clay in the Ashanti Region attains pozzolanic nature at 900°C. He used the produced pozzolana to replace between 25 to 30% of Portland cement and found that, the mortars produced and cured under water for 28 days were comparable to that of the unblended mortar mix. In a recent study, Momade and Atiemo (2004) replaced Portland cement by 30% pozzolana produced from Hwereso and Asokwa in the Ashanti Region, Nkosia and Mankessim in the Central Region. They concluded that the mixture between the Portland cement and pozzolana produced between 33.5MPa and 34.7MPa which was higher than the minimum requirement of 32.5MPa as prescribed by the European standards.

The investigations carried so far in Ghana on clay pozzolana have been very general for construction and therefore the need to investigate into the utilization of pozzolana for specific works like masonry cement formulation and others remain very vital.

Other agricultural by-products have been investigated and found to improve the strength of concretes and mortars. Sata *et al* (2007) found that the compressive strength of concretes at 28 days with 10-20% rice husk or bark ash were higher than the control by about 9 to 13%. Similar results were also observed by Zhang & Malhotra (1997) and Ismail & Waliuddin (1996).

Silica fume which is described as a super pozzolanic material has also been found to increase the strength of mortar containing 5-25% silica fume compared with the plain mortar (Kohno *et al*, 1989). Rao Appa (2003) reported that with 0.45 water- to- binder ratio and 30% silica fume, the resulting binder paste exhibited higher strength between 1 and 180 days. Moreover, Yogendra *et al* (1987) and Hooton (1993) reported that the optimum silica fume content to produce higher strength mortar ranges between 15 and 20% at 28 days of curing at water- to- cement ratio of 0.5. On the contrary, Sabir (1995) showed that the optimum silica fume content to produce high mortar strength was 28% at different water- to- cement ratio of 0.4.

Pozzolanic materials are known to retard early strength but improve the late strength development of mortar and concretes (Wei *et al*, 1985 and Swamy, 1990). However some researchers have shown that some pozzolanic materials improve strength development on the first day of curing. After the first day of curing, the strength retards until probably 14 days of curing. In the work of Wild *et al* (1996), it was shown that the maximum strength was obtained with 10% metakaolin on the first day. The maximum strength fell linearly as the percentage of metakaolin content increased. Strength development between 5 and 30% of metakaolin content were better than the plain mortar at 90 days. In their explanation to this, they attributed the early strength at 10% of metakaolin to the filler effect and the decrease in strength with increased metakaolin content as being due to dilution effect. Agarwal and Gulati (2006) also made similar explanation to this effect. Sata *et al* (2007) attributed the late strength development of pozzolanic materials not only to pozzolanic properties which chemically react with $Ca(OH)_2$ but also to packing density. In the explanation given by Rao Appa (2003), he attributed the high strength of pozzolanic materials to pore size refinement and matrix densification, reduction in calcium hydroxide and cement paste aggregate interfacial refinement. Feldman *et al* (1985) also gave similar explanation in his work on properties of silica fume paste. Pozzolanic effect is further explained in the hydration process between Portland cement and pozzolana.

2.6.5.2 Water demand of blended pozzolana paste

Pozzolanas produced from calcined clays, silica fume and agricultural waste are known to increase the water required to form a workable mortar or concrete. From investigations by Samet *et al* (2007), water- cement ratio for normal consistency of mortar increased from 27% to 31% by adding calcined clay. Uzal and Turanli (2003) also realized that natural pozzolana addition to cement increased the water demand for a workable mortar by 50% when compared to ordinary Portland cement. Rao Appa (2003) showed that the water demand for 30% silica fume and 70% ordinary Portland cement binder paste was found to be 44.25% whilst that for OPC paste was 31.50%.

A recent work investigated by Naceri and Chikouche Hamina (2009) on the use of waste milled brick as a partial replacement of cement in mortar at 5,10, 15 and 20% showed that the water required to have a workable paste was increased more than in the plain cement paste. They also noticed that the progressive addition of pozzolana (milled waste brick) influenced appreciably the water demand. This result showed that the water demand which was progressively increased was a function of the percentage pozzolana addition.

Moreover, Badogiannis *et al* (2005) replaced Portland cement (PC) with metakaolin at 36, 37, 49 and 71% of PC. Their results showed that the blended cements demanded significantly more water than the relatively pure cement. Samet *et al* (2007) explained this by using the fineness and porosity of calcined clays as being responsible for the increase of water demand. Similarly, Rao Appa (2003) explained that, the rise in water demand for silica fume binder paste was due to the higher fineness value.

Water demand for fly ash behaves differently, that is, it rather decreases the water demand. The work of Chindaprasirt *et al* (2004) showed that incorporation of fly ash reduced water- binder ratio as compared to ordinary Portland cement mortars. Again earlier investigation by Pandey *et al* (2003) found that increasing percentage fly ash content from 20 to 35% decreased the water requirement. Chindaprasirt *et al* (2004) reported that the reduction in water demand was due to the spherical and the smooth surface of fly ash which helped the flow and workability of the mix.

2.6.5.3 Setting time of blended pozzolana paste

The effect of pozzolanic materials used as ordinary Portland cement substitutes increases the setting times of mortars and concretes (Brooks *et al*, 2000). This effect has been well documented in many research papers.

Clay pozzolana which was investigated by Samet *et al* (2007) was found to cause an accelerating effect on the setting of mortar when ordinary Portland cement was replaced by 30% pozzolana content. The result of Morsy *et al* (1997) showed that thermally activated kaolinite clay prolonged the initial and final setting times.

Naceri and Chikouche Hamina (2009) analyzed the effect of waste clay brick used as a pozzolana on the setting times of the blended paste. They replaced Portland cement with pozzolana at 5, 10, 15 and 20%. Their results showed that the setting times at all replacement level decreased as compared to the plain paste. There was also a progressive decrease in both initial and final setting times as the pozzolana addition increased.

The inclusion of metakaolin in ordinary Portland cement (OPC) paste at 5, 10 and 15% of OPC was investigated by Brooks and Johari (2001). Their results showed that an increase in metakaolin caused an increase in the setting times as shown in Table 2.8.

Table 2.8: Setting times of plain and blended pozzolana paste

Mix	initial setting time	Final setting time
OPC	5.0	7.7
MK5	6.42	8.82
MK10	6.98	9.42
MK15	6.45	9.31

The effect of fly ash addition in ordinary Portland cement mortars was determined by Naik and Singh (1997). They found that replacement of 30% fly ash in the mortar increased the setting time from 1.6 to 2.3 hours. Fu *et al* (2002) replaced clinker by fly ash at 45, 51 and 60%. They also recorded relatively higher setting time both initial and final than the plain cement paste.

Other pozzolanic materials like agricultural ash and silica fume also behave in a similar manner as clay pozzolana and fly ash. Alshamsi *et al* (1993) showed that the use of silica fume as partial ordinary Portland cement replacement extended the setting times of pastes with greater retardation at higher replacement level. Similar results were also obtained by Wang *et al* (2001) in their investigation on amorphous silica residue as supplementary cementing materials. However, in the studies of Rao Appa (2003), the initial setting time was rather affected by silica fume replacement level (5-30%) whereas the final setting time seemed not to be affected.

The retardation of setting time when pozzolanic materials are used to replace some portions of ordinary Portland cement has been explained by Brooks *et al* (2000) and *Fu et al* (2002). Whilst Brook *et al* (2000) attributed the effect to lower ordinary Portland cement content which causes slower stiffening of mortars; Fu *et al* (2002) explained it by using the lower pozzolanic effect which occurs at a slower rate.

2.6.6 Limestone blended cement

Limestone is an important calcareous filler or mineral admixture for cement mortar manufacture. The addition of limestone to ordinary Portland cement gives Portland limestone cement. Limestone powder has been used to produce cement in some countries, and in the recent EN 197-1 specification, up to 35% of limestone powder can be added to produce Portland limestone cement and Portland composite cement (Zhu and Gibbs, 2005). The addition of limestone to ordinary Portland cement may significantly improve several cement properties such as compressive strength, water demand, workability and durability (Cochet and Sorrentino, 1993; Livesey, 1991).

According to Heikal *et al* (2005), limestone can be inert and serve as filler, be slightly hydraulic or have pozzolanic properties. Fillers affect strength by accelerating the cement hydration especially the early strength.

In Ghana, Orterkpolu limestone deposit is now mined by Ghana Cement manufacturers (Ghacem) for the production of Portland Limestone cement (PLC). The production of PLC by Ghacem utilizes between 15 and 20% of the limestone powder which is blended together with Clinker and gypsum in a Ball mill.

2.6.7 Chemical and mineral composition of limestone

Limestone is a naturally existing mineral that consists principally of calcium carbonate ($CaCO_3$). Limestone is a sedimentary rock and its chemical composition and purity vary according to the sedimentary environment. The purity of limestone is classified into 3 groups.

1. High calcium limestone ($CaCO_3$>95%)
2. High magnesium dolomite ($MgCO_3$>42%)
3. High purity carbon ($CaCO_3$ & $MgCO_3$>95%)

The chemical composition of limestone varies widely depending on the route by which it was obtained. Standard EN 197-1(1993) requires that, in Portland limestone cement, the limestone should contain at least 75% $CaCO_3$ by weight, with less than 1.2% clay and less than 0.2% organic material.

The principal mineral found in limestone is calcite with dolomite and aragonite forming minor mineral component (Hurlbut, 1971). Figure 2.4 shows an example of X- ray diffraction results of limestone powder which was determined by Benachour *et al* (2008). The results indicate the presence of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$).

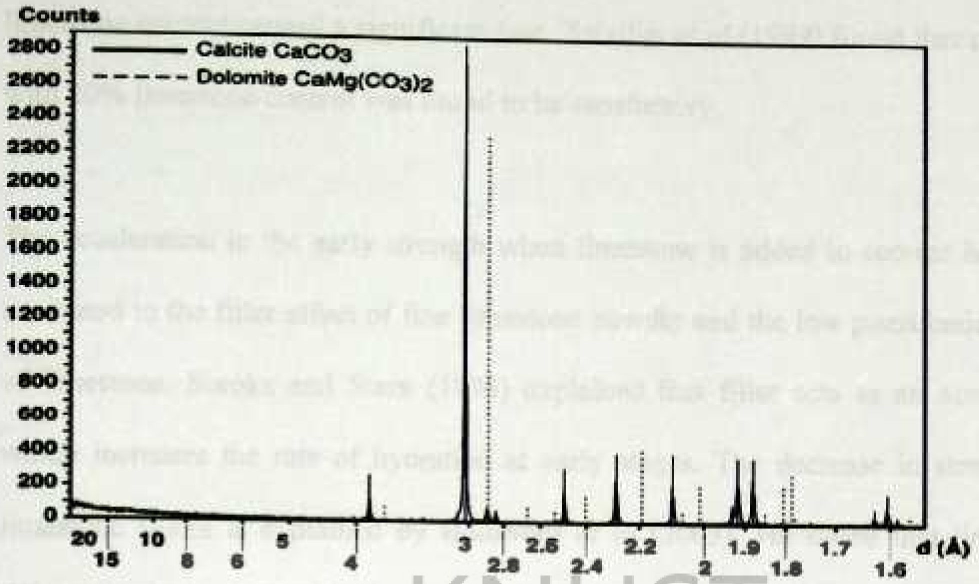

Figure 2.4: X- ray diffraction results for limestone powder showing the presence of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$)

2.6.8 Mechanical properties of limestone blended cement

2.6.8.1 Compressive strength

The strength development characteristics of Portland limestone cements are different from those of other composite cements. Voglis *et al* (2005) made a comparative study on Portland limestone cement (PLC), Pulverized fly ash cement (PFC), Portland pozzolanic cement (PPC) and Portland cement (PC) using 15% content of limestone, fly ash and natural pozzolana, respectively. They concluded that PLC exhibited a higher early strength (7 days). However it was found that PLC recorded the lowest strength development at later ages (28-540 days).

Earlier findings by Nedhi and Mindess (1996) showed that up to 10-15% cement replacement did not affect mortar strength at the early age, however higher levels of limestone content caused a significant loss. Tsivillis *et al* (1999) found that concrete with 20% limestone content was found to be satisfactory.

The acceleration in the early strength when limestone is added to cement has been attributed to the filler effect of fine limestone powder and the low pozzolanic nature of limestone. Soroka and Stern (1976) explained that filler acts as an accelerator which increases the rate of hydration at early stages. The decrease in strength of limestone fillers is explained by Bonavetti *et al* (2003). He stated that limestone fillers do not have pozzolanic properties, but it reacts with the alumina phases of cement to form calcium monocarboaluminate hydrate at the early stage of cement hydration.

2.6.8.2 Water demand for limestone blended paste

Tsivillis *et al* (2002) in their analysis of the properties of Portland limestone cements and concretes realized that limestone cement demanded less water than relatively pure cement. They replaced cement clinker with limestone at 10, 20 and 35% at different milling times at 38, 45, 52 and 60 minutes in a ball mill. Table 2.9 shows the results of the work that was investigated by Tsivillis *et al* (2002). From the results, it is seen that the blended paste demanded less water than the plain paste which is also termed as the control (C). Water demand was also found to decrease with increasing limestone content in the paste. The grinding time was found not to have much significant effect on the paste water demand.

Table 2.9: Paste water demand for Portland cement and Portland limestone cement at different milling times

Portland cement	Paste water demand (%)
C- 38	26.0
C-45	26.0
C- 52	25.7
C- 60	25.7
Portland limestone cement	
CL-10- 38	25.4
CL-10- 45	25.0
CL-10- 52	25.0
CL-10- 60	25.1
CL-20- 38	23.5
CL-20- 45	23.2
CL-20- 52	23.2
CL-20- 60	23.4
CL-35- 38	22.9
CL-35- 45	22.8
CL-35- 52	22.8
CL-35- 60	23.1

Source: Tsivillis *et al*, 2002

Voglis *et al* (2005) in their studies compared Portland limestone cement to other blended mixtures such as Portland fly ash and Portland pozzolana cement and found that at 15% of the composite material (limestone, fly ash or pozzolana) replacement, Portland limestone cement (PLC) water demand was 24.5% which was less than that of Portland pozzolana cement (PPC) and Portland fly ash cement (PFC) which were 26.2% and 26.4% respectively. The water demand for Portland cement was 24.3% which is less than the blended cement paste labeled as PLC, PPC and PFC which were 24.5%, 26.2% and 26.4% respectively.

On the contrary, a study conducted by Helal (2002) found that addition of limestone content from 5%-20% increased the amount of water required for a good consistency. He gave the reason as being due to the high water absorption capability of limestone.

2.6.8.3 Setting time of limestone blended paste

The utilization of limestone as a mineral admixture to replace a percentage of OPC generally decreases or results in similar setting times of the control paste. Heikal *et al* (2000) found that up to 20% weight limestone replacement caused reduced initial and final setting times. It was also indicated by Vuk *et al* (2001) that the addition of limestone exhibited a strong effect on the initial and final setting times measured by the Vicat apparatus. They said limestone addition at 10, 15, 20 and 30% decreased both initial and final setting times.

They attributed the reason for the decrease in the setting times to the amount of tricalcium silicate (C_3S) quantity in cement. Their results showed that between (35 and 45%) of C_3S, the setting times occured faster. However results obtained by Voglis *et al* (2005) showed that using 15% weight of limestone did not indicate any significant difference compared to the control paste. This was also found by Tsivilis *et al* (2002) when they replaced OPC by 10, 20 and 35% by weight of limestone.

Table 2.10 represents results of the studies of Voglis *et al* (2005) on the use of 15% of limestone, fly ash or natural pozzolana and 85% of ordinary Portland cement.

Table 2.10: Setting times of PC, PLC, PPC and PFC

Sample	Setting times (min)	
	Initial	Final
PC	125	170
PLC	90	170
PPC	95	140
PFC	100	160

PC: Portland cement; PLC: Portland limestone cement; PPC: Portland pozzolana cement; PFC: Portland fly ash cement

Source: Voglis *et al*, 2005

Kakali *et al* (2000) investigated the hydration products of C_3A, C_3S and Portland cement in the presence of calcium carbonate ($CaCO_3$). Table 2.11 shows the results of their setting times. It is shown from the table that the initial and final setting times of limestone cement (LC) paste at 10% increased, however, at 20% to 30%, it decreased.

Table 2.11: Setting times of limestone blended paste

Sample	Setting times	
	Initial	Final
LC- 0	140	190
LC- 10	145	195
LC- 20	110	180
LC- 30	100	165

LC: limestone cement

It has been reported by Heikal *et al* (2000) that the effect of limestone in cement paste is partly physical and partly chemical. The decrease in the initial and final setting times could be attributed to the fact that limestone enhances the formation of calcium hydroxide at early ages because it provides nucleating sites for its growth.

2.6.9 Slag as substitute material for Portland cement

Ground granulated blast furnace slag (GGBS), steel-making slag which is another form of cementitious materials are commonly used in combination with Portland cement to make concrete and mortar for many applications (Escalante-Garcia and Sharp, 2001). The use of slag as a constituent of concrete was first recorded in 1905 (Craig Duos and John Eggers, 1999). The European Standard ENV 197-1: 1992 recognizes three classes of Portland slag cement called slag cement III/A, III/B, III/C. All of them differ in percentages of the mass of the cementitious material with about 5 percent of filler. The slag percentages are as follows:

Class III/A	36 to 65
Class III/B	66 to 80
Class III/C	81 to 95

(Source: Neville, 1996)

Slag has been used in conjunction with Portland cement to produce masonry cement in places like France and Belgium since 1958 (Lea, 1970).

2.6.10 Chemical composition of slag

Chemically slag is a mixture of lime, silica and alumina. Blast furnace slags possess slightly different chemical composition from steel making slags. Blast furnace slags, with the following percentages of composition is satisfactory in cement.

Lime (CaO)	40 to 50
Silica (SiO_2)	30 to 40
Alumina (Al_2O_3)	8 to 18
Magnesia (MgO)	0 to 8
Sulphur (S)	1 to 2.5

(Source: Lea, 1970)

The chemical composition of steel slag as reported by Shi and Qian (2000) is as follows;

CaO 45-60%, SiO_2 10-15%, Al_2O_3 1-5%, Fe_2O_3 3-9%, FeO 7-20%, MgO 3-13% and P_2O_5 1-4%.

2.6.11 Mechanical properties of blended slag cement

It is generally recognized that the rate of hardening of Portland blastfurnace slag cement in mortar or concrete is somewhat slower than that of ordinary Portland cement during the first 28 days, but thereafter increases so that at 12 months the strength comes close to or even exceeds those of Portland cement (Lea, 1970). Slag is normally not used in applications where high early age strength is required

(Barnett *et al*, 2006). Altun and Yilmaz (2002) have reported that blended cements containing 15-30% steel slag developed between 66 and 83% of plain cement strength at 28 days. In the study by Kourounis *et al* (2007), between 15 and 30% slag content in Portland cement produced 72 to 88% of cement strength at 28 days whereas at 90 days the strength was between 80 and 92% respectively.

The water demand for slag-blended cements was found to decrease with increasing percentage slag replacement (15, 30 and 45%) in the studies of Kuorounis *et al* (2007). They attributed this effect to the delayed hydration of slag due to the mineralogical composition which is probably the presence of MgO.

Slag application in Portland cement extends the setting times (initial and final) of mortar and concretes in most cases. The test results of Eren *et al* (1995) indicated that the use of slag up to 50% replacement level increased the setting time of concrete at room temperature. This was also confirmed by Brooks *et al* (2000) who stated that blast furnace slag retards the setting time of high-strength concrete. Other authors, however, have reported that some types of slag such as silicomanganese slag when blended with cement showed little effect on the initial and final setting times. For example, the work by Frais *et al* (2006) found that at 10 and 15% SiMn slag content, the setting times (initial and final) were not different from the plain mortar. The setting time delay in most blended slag cement was explained by Kourounis *et al* (2007) as due to dilution effect which again results in a slowdown of hydration. However, other authors have associated this to low Al_2O_3, high MnO and MnO_2 content in slag (Altun and Yilmaz, 2002; Rai *et al*, 2002). Pera *et al* (1999) have illustrated that high levels of MnO seem to inhibit the early age hydration of cement but have no negative effect on the long term properties.

2.7 Ternary blended cements

Ternary blended cement mortar is defined as the combination of clinker and two other cementitious mineral admixtures (Elkhadiri *et al*, 2002). The formation of ternary blend is reported by Carrasco *et al* (2005) as dependent on the available mineral resources that can be found in each country. The formulation could be between clinker and any other two of the following: pozzolan, metakaolin, slag, fly ash, silica fume and limestone.

In some parts of Australia, ternary and even quaternary cements have been intermittently been available since 1966 (Thomas *et al*, 1999). In a quarternary blend, ordinary Portland cement is combined with three other cementitious mineral materials. In Canada, ternary blended cement including a combination of silica fume and fly ash is currently being produced by a cement company in Joillette, Quebec. Ternary blend of silica fume and slag is also being produced in St.Constant, Quebec (Bouzoubaa *et al*, 2004).

It is reported that ternary blended mortars present many technical advantages than binary mortars. Carrasco *et al* (2005) and Nedhi (2001) have reported that ternary blend allows the compensation of mineral admixtures shortcomings by their synergistic effect within the ternary mixture. An example is the effect of a pozzolan at the early stages of hydration which is very slow compared to Portland cement and limestone mixtures which are faster at the early stages but cause strength reduction at later ages. The strength reduction which is caused by the presence of limestone is attributed to the production of free lime which has the ability to dilute the effect of calcium silicate hydrate formed after cement hydration. The strength gain depends primarily on the formation of calcium silicate hydrates (Heikal *et al*, 2000).

2.7.1 Mechanical properties of ternary blended mixtures

In recent years many authors have reported that the combination of a filler material and a pozzolanic material results in better mechanical properties of mortars and concrete than binary mixes (Shehata and Thomas, 2002; Khan and Lynsdale, 2000 and Bai *et al*, 2000).

A ternary mixture which used blast furnace slag and limestone was investigated by Carrasco *et al* (2005). They concluded from their findings that the combination of blast furnace slag, limestone and cement produced an optimum strength better than binary mixtures. While the limestone improved the early age strength, the slag improved the late strength development (Lawrence *et al*, 2003). Similar results were obtained by Menedez *et al* (2003) in their investigations on strength development of ternary blended cement with limestone filler and blast-furnace slag.

Elkhadri *et al* (2002) investigated the combination of fly ash and limestone in a ternary blend system. They found that as the limestone gave a good early hydration the fly ash also contributed its effect on the strength after 28 days.

Ghrici *et al* (2007) made a study on ternary mixture comprising natural pozzolana and limestone. They reported that the point of maximum strength at early age of hydration was with 10% limestone and low natural pozzolana. After 28 days, strength gain moved toward the high level of natural pozzolana and low limestone filler content.

Earlier investigations by Heikal *et al* (2000) on limestone- filled pozzolanic cement showed that the addition of limestone decreased the compressive strength of pozzolanic mortars. The strength reduction was attributed to the dilution effect from the limestone addition which means that at some contents of limestone, some portion of it remains un-reacted in the mix.

Heikal *et al* (2000) further investigated the setting time effect using limestone and natural pozzolana in ternary blend system. They found that increasing limestone content to 20% reduced the setting time.

2.8 Hydration of Portland cement and blended cements

2.8.1 Portland cement hydration

Cement clinker particle is a multiphase solid having massive calcium silica grains (50-100μm) in a matrix of interstitial aluminate and ferrite. The main mineral composition of Portland cement is tricalcium silicate (C_3S), dicalcium silicate (C_2S) and tetracalcium aluminoferrite (C_4AF). Gypsum (Calciumsulphate hydrate, $CaSO_4.2H_2O$) is added in a minor proportion (1 to 3%) to control the setting of cement (Lasic, 1989).

When Portland cement or blended cements and water are mixed together hydration occurs. The hydration process is characterized by setting and hardening processes, which have a complex chemical reaction. Setting is identified with certain stage in the development of coagulational- crystallization network, initially weak and thixotropic, while the process of hardening denotes the development of the much stronger irreversible, crystalline structures (Lea, 1960). During the hydration process, each mineral component has some specific reaction with water. Some reactions are very fast and others are slow.

Greene (1960) demonstrated that the aluminate phases and gypsum undergo the fastest reactions when water is added to cement. High-calcium sulphoaluminate hydrate ($3CaO.3Al_2O_3.3CaSO_4.32H_2O$) that is formed in solution is also known as ettringite. Ettringite binds up water and these affect hydration. Later low-sulphate calcium monosulphoaluminate hydrate ($3CaO.3Al_2O_3.CaSO_4.12H_2O$) is formed in the solid phase. The aluminate reaction that occurs in the presence of gypsum solution is indicated by Lasic (1989) below:

$$3CaO.Al_2O_3 + 3CaSO_4.6H_2O + 26H_2O \rightarrow \underset{\text{ettringite}}{3CaO.Al_2O_3.3CaSO_4.32H_20}$$

This reaction is exothermic and contributes a little to the ultimate strength but more to the early hydration and setting of cement products (Lea, 1970). Other aluminate hydrates are formed which may exist separately or in solid state with the monohydrate.

C_3S and C_2S reactions occur concurrently with C_3A reaction. The reaction produces crystals of calcium hydroxide [$Ca(OH)_2$] also known as portlandite together with nearly amorphous calcium silicate hydrates (CSH). The CSH produced by both C_3S and C_2S are the same however little $Ca(OH)_2$ is produced by C_2S. The CSH produced is the principal binding phase in Portland cement and is quantitatively the most significant hydration product (Lea, 1960).

$$\underset{(C_3S)}{2(3CaO.SiO_2)} + 6H_2O \rightarrow \underset{(CSH)}{3CaO.2SiO_2.3H_2O} + \underset{\text{Portlandite}}{3Ca(OH)_2}$$

$$\underset{(C_2S)}{2(2CaO.SiO_2)} + 4H_2O \rightarrow \underset{(CSH)}{3CaO.2SiO_2.3H_2O} + \underset{\text{Portlandite}}{Ca(OH)_2}$$

The ferrite reaction also has an important long term contribution to strength and durability. Portland cement, if fully hydrated produces $Ca(OH)_2$ or portlandite of about 28% of its own weight. However in practice, in fully mature concrete, portlandite would not normally exceed 20% (Sabir *et al*, 2001). $Ca(OH)_2$ liberated by the hydration of Portland cement does not make any significant contribution and can be harmful to concrete and mortar durability. Rao Appa (2003) has reported that the morphology of $Ca(OH)_2$ crystals are relatively weak, brittle and not cementitious.

2.8.2 Pozzolanic reaction

The principal reaction of pozzolanas and Portland cement occurs between the silicates and aluminates present in pozzolana and the calcium hydroxide released from cement hydration in the presence of water. Silica and alumina go into solution quickly, reacting to form two products, tetracalcium aluminate hydrate and calcium silicate hydrate (Singh and Garg, 2006).

It has been shown by Lea (1938) that zeolitic structures found in volcanic tuffs (natural pozzolanas) are quickly attacked by $Ca(OH)_2$ through base exchange. According to Lea (1970), zeolites are defined as a group of insoluble hydrated alumino- silicates of the alkalis and alkaline earths which have the property of exchanging some of their base constituents for others when immersed in solution.

Calcined clay materials (metakaolin) behave the same way like zeolitic structures. It undergoes total dehydration by heat treatment and makes the bonds between silica and alumina relaxed or annihilated.

The reaction of calcined clay and Portland cement occur between the metakaolinite ($Al_2O_3.2SiO_2$) and calcium hydroxide ($Ca(OH)_2$) from cement hydration. This reaction forms additional cementitious aluminuim containing calcium silicate hydrate (CSH) gel, together with crystalline products, which include calcium aluminate hydrates and alumino-silicate hydrates (i.e. C_2ASH_8,C_4AH_{13} and C_3AH_6) (Sabir et al, 2001). Singh and Garg (2006) in their work on reactive pozzolana from Indian clay pozzolana in cement mortars produced the following equation:

$$Al_2O_3.2SiO_2 + 5\,Ca(OH)_2 + 19H_2O \rightarrow Al_2O_3.4CaO.19H_20 \quad + \quad CaO.2SiO_2.H_20$$

Metakaolin Lime Water Tetracalcium aluminate Calcium silicate hydrate
hydrate

According to Murakami (1952), the presence of reactive alumina considerably enhances the mechanical strength of pozzolanic cements particularly for brief curing. In addition, if carbonate is freely available carbo-aluminates may also be produced.

2.8.3 Hydration of Portland cement containing limestone

The addition of limestone either as filler or mineral admixture to cement is reported to have good performance [Aitcin (1996)]. First, it is believed that $CaCO_3$ accelerates the C_3S hydration, particularly as the $CaCO_3$ becomes finer and its addition rate is increased (Ramachandran and Chun-Mei, 1986). $CaCO_3$ also enhances the formation of calcium hydroxide, probably because it provides nucleation sites for its growth (Barker and Cory, 1991) as already mentioned. Pera *et al* (1999) reported that as silicate hydration is accelerated, early strength of paste is obtained. This is also confirmed by Ingram and Daugherty (1992).

Secondly, $CaCO_3$ is believed to react with C_3A in the presence of water to form low calcium carboaluminates [$C_3A.CaCO_3.10\text{-}11H_2O$] (Feldman *et al*, 1965). The carboaluminates are formed in suspensions and pastes of C_3A, C_4AF, or cement in the presence of calcium or magnesium-carbonate. Cement strength is known to increase due to the formation of low carboaluminates (Turker *et al*, 2004). In the investigation by Ramachandran (1988), he found that the conversion of ettringite to the hydrate form is accelerated by $CaCO_3$. Ettringite, monosulphate and monocarboaluminate can all exist in the Portland cement system.

Heikal *et al* (2000) reported that, the carbonate ion (CO_3^{-2}) should be regarded as an important factor in the hydration of C_3A in the presence of calcium sulfate and $Ca(OH)_2$. Limestone addition to cement does not remove portlandite or $Ca(OH)_2$ from paste at later age (Irrasar *et al*, 2000) but rather increases the $Ca(OH)_2$ liberated from cement paste. Sersale (1992) indicated that limestone does not have pozzolanic properties and also does not produce calcium silicate hydrate which is a significant hydration product.

2.9 Durability studies of Portland cements and blended masonry mortars

Durability is an important engineering property of mortar and concrete. It determines the life span of mortar and concrete very significantly. Due to the interactions of mortar and concretes with external influences, their durability may be threatened and lost. The threatening factors to mortar and concretes are many. Among the threatening factors reported in past studies are freezing and thawing, abrasion, corrosion of steel and chemical attacks (Zivica and Bajza, 2001).

The American Concrete Institute (ACI) committee (1982) has classified chemical attack into (i) acidic attack (ii) alkali attack (iii) carbonation (iv) chloride attack (v) leaching and (vi) sulphate attack. Each chemical attack is a subject of document reported by many authors. It has been reported by Chindaprasirt *et al* (2004) that one of the most important aspects of durability of mortar and concrete is the resistance to sulphate attack. It is stated that sulphate attack on mortars and concrete is a complex process (Cohen and Mather, 1991). Sulphate attack could be as a result of internal and external sources. Internal sulphate attack could be related to different forms of calcium sulphates added to clinker during cement grinding as part of cement.

External sulphate attack is generally related to natural sulphates of calcium, magnesium, sodium and potassium present in soils or dissolved ground water.

Sulphate attack in most mortars and concretes has been attributed to the presence of un-reacted $Ca(OH)_2$. However other authors too relate this effect to high content of C_3A and C_4AF in cement clinker (Irassar *et al*, 2000). $Ca(OH)_2$ released is due to the presence of C_3S and C_2S minerals in clinker and reported already that about 30% $Ca(OH)_2$ is found in a fully matured mortar and concrete (Sabir *et al*, 2001). $Ca(OH)_2$ are normally vulnerable to sulphate attack which creates damages to mortar and concrete.

Portland cement- based materials subjected to attack from sulphate may suffer from two types of damage: loss of strength of the matrix due to degradation of hydrated calcium- silicate and volumetric expansion due to the formation of gypsum or ettringite that leads to cracking (Mobasher *et al*, 2007).

Previously, several researchers have confirmed that limitations on C_3A and C_4AF content are not the ultimate answer to the problem of sulphate attack (Cohen and Bentur, 1988). Blended cements containing active mineral admixture (fly ash, slag, silica fume or natural pozzolana) have demonstrated to be sulphate resistant. The ability of these pozzolanic materials in blended cement to resist sulphate attack is explained by three main factors: Pore size refinement, C_3A dilution and $Ca(OH)_2$ removal (Tikalsky and Carrasquillo,1990).

Fillers like limestone which are also used in blended cement however do not confer equivalent properties like pozzolanic materials. Filler addition does not remove $Ca(OH)_2$ or portlandite at later ages. Higher forms of portlandite liberated in Portland limestone cements are susceptible to sulphate attack (especially, thaumasite formation $\{Ca_6[Si(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2\})$ for severely aggressive environment (Hartshorn *et al*, 1999 and Hartshorn *et al*, 2001). In recent times, it has been reported that the amount of C_3A in Portland cement is accelerated by $CaCO_3$ to form secondary ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) and gypsum (Ingram and Daugherty, 1992).

The involvement of limestone in the thaumasite form of sulphate attack has been identified as a major factor responsible for mortar and concrete deterioration. It has been reported that the extent of formation of thaumasite ($Ca_6[Si(OH)_6.12H_2O]_2(SO_4)_2(CO_3)_2$) is greater with increasing limestone content in cement (Torres *et al*, 2003). Other authors have analyzed durability by using the rate of water absorption in mortars. It has been explained by Elinwa and Ejeh (2004) that the rate of moisture rise in mortars describes how dense the mortar is and that the higher the moisture rise the less dense the mortar structure and vice versa.

2.10 Availability of clay and limestone in Ghana

2.10.1 Clay

The engineering definition of clay is a fine-textured soil with colloidal in size grains, composed mainly of hydrated silicate of aluminium mixed with various impurities. It is plastic and cohesive, shrinks when dry, expands when wet, gives up its water when compressed and gains in strength with retention of shape on firing (Ayetey, 1977). Large deposits of clay exist in higher quantities all over Ghana (Kesse, 1985). Table 2.12 represents the various regional deposits and their tonnages. Figure 2.5 also shows the location of the clay deposits in Ghana.

Table 2.12: Clay deposit in Ghana

Region	Tonnage(million)
Central	106
Greater Accra	200
Eastern	90
Western	742
Ashanti	39
Brong Ahafo	17
Volta	165
Northern	11
Upper East and West	22

Source: Kesse, 1985

As already mentioned, most of the clay deposits have not attracted extensive studies, with the exemption of a few deposits like Hwereso, Mankranso, Mfensi and Asokwa all in Ashanti Region as well as some part of clay from Mankessim in the Central Region. Moreover the studies of Atiemo (1994) is limited to the suitability of pozzolana production from some clay site in Ashanti Region (Hwereso, Mfensi and Asokwa) and some small area in the Central Region (Mankessim and Nkosia).

The need to investigate other clay deposits in Ghana as well as utilizing clay pozzolana for specific works like concrete, plastering, rendering and jointing of blocks or bricks is needed and important.

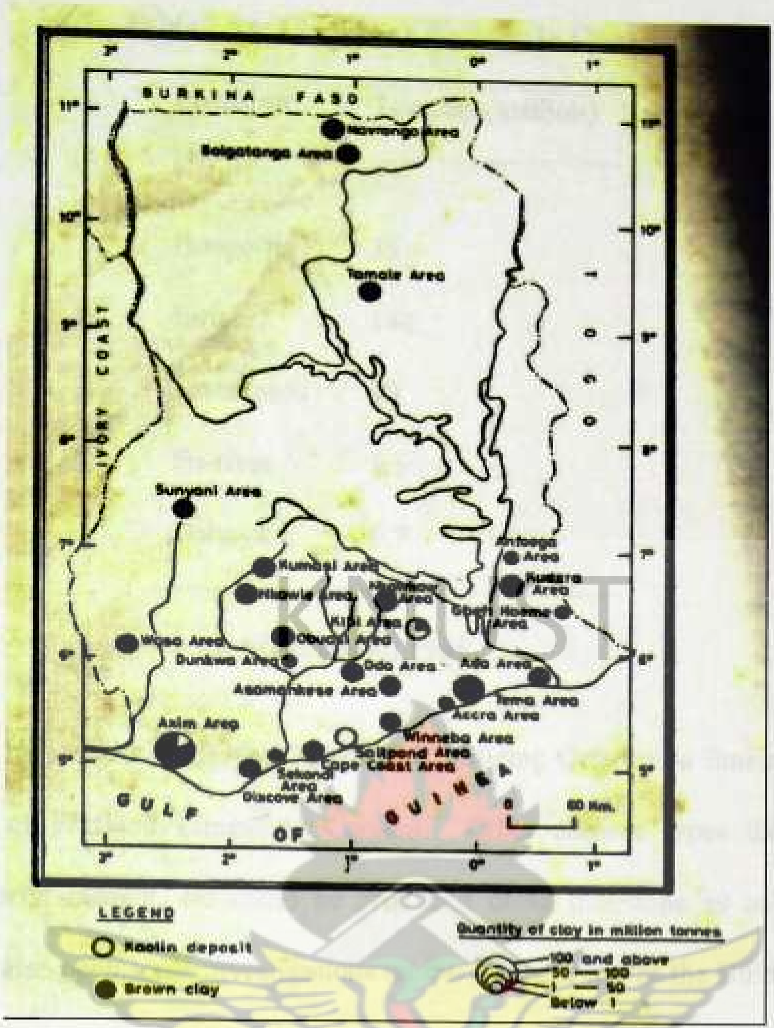

Figure 2.5: Map of Ghana showing clay deposits

Source: Kesse, 1985

2.10.2 Limestone

Limestone can be defined as a sedimentary rock composed chiefly of calcium carbonate ($CaCO_3$). A review of the limestone deposit has identified some areas in Ghana where it is located. They are Bonga-da, Buipe and Daboya in the Northern region, Orterkpolu in the Eastern region, Nauli in the Western region and Fo-river in the Central region. Table 2.13 and Figure 2.6 show the quantites and locations in Ghana.

Table 2.13: Limestone deposits in Ghana

Location	Tonnage(million)
Nauli	23
Bongo-da	35
Buipe	144
Orterkpolu	10
Fo-river	1.5
Daboya	0.7

Source: Kesse, 1985

It has been indicated already that, Ghacem is utilizing Orterkpolu limestone for the production of Portland Limestone Cement. Other cement types like Masonry cement, Mortar cement, etc could be produced using limestone as an admixture. There have also been some investigations on the potential use of the Buipe limestone deposit for the production of Portland cement which has not been finalized. With the exception of the Orterkpolu and Buipe limestone deposit, the other limestone deposit has not been investigated for their potential use in the construction industry.

Though Ortekpolu limestone deposit is already being mined by Ghacem for the production of Portland limestone cement (PLC), there is also the need to investigate into the use of that limestone powder for masonry works like plastering, rendering and jointing of blocks or bricks and probably for concrete works.

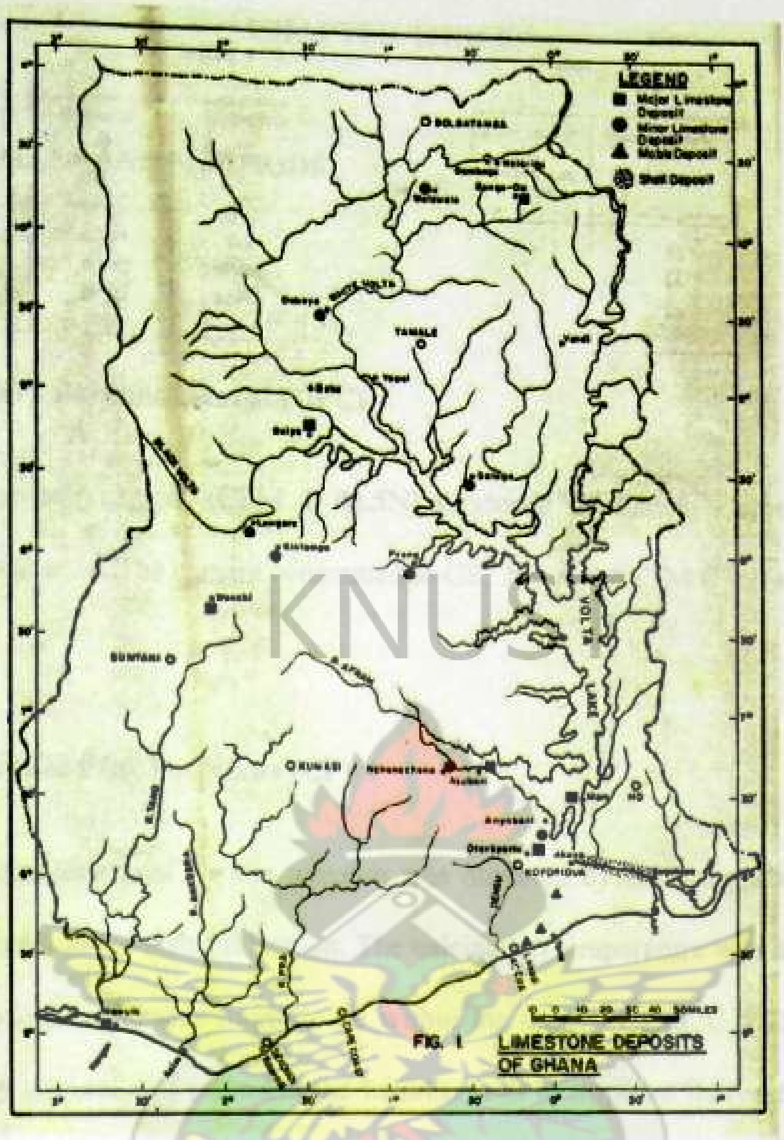

Figure 2.6: Map of Ghana showing limestone deposits

Source: Kesse, 1985

CHAPTER THREE

3.1 MATERIALS AND METHODS

3.2 Materials

3.2.1 Ordinary Portland cement (OPC)

Ordinary Portland cement (CEM 1 42.5N) produced by Ghana Cement Works (Ghacem) was used. The cement conformed to GS: 766 and ASTM C150 standards.

3.2.2 Mankranso Clay Pozzolana (CP)

The Clay pozzolana used for the research was obtained by calcining clay mineral from Mankranso in the Ashanti Region. The calcination temperature was determined by a thermocouple and was found to be within the range of 650 °C to750°C. The calcined clay mineral was milled in the hammer mill to improve its reactivity with Portland cement. Fineness of the clay pozzolana was determined as specified by ASTM C184 using 75µm sieve size.

3.2.3 Limestone (L)

The limestone used was obtained from Orktepolu in the Eastern region of Ghana. It is a whitish rock. The limestone was crushed into smaller particle sizes by a jaw crusher after which a hammer mill was used to mill it. Fineness of the limestone was also checked as specified by ASTM C184 using 75µm sieve size.

3.2.4 Natural Sand

Natural graded sand was used for the mortar mixes and complied with BS 4550: Part 6 requirements. The sand was sieved passing 850 μm test sieve and retained on 600 μm test sieve.

3.3 Methods

3.3.1 Physical characterization.

The following physical characterizations of the materials (OPC, CP and L) were determined:

- Particle size analysis
- Specific gravity
- Blaine fineness

3.3.1.1 Particle size analysis and specific gravity

Particle size analysis was determined using the sedimentation test method which is in accordance with BS 1377. About 300g of air-dried sample was oven-dried for about 6hrs at 105°C. 50g of the oven-dried sample was taken and transferred into a 600 ml brass container. A dispersant solution composed of sodium carbonate anhydrous, sodium hexametaphosphate powder was prepared. The dispersant solution was prepared by mixing 7g of sodium hexametaphosphate and 33g of sodium oxalate which was diluted to 1000 ml by distilled water in a measuring cylinder. 100ml of the dispersant solution was added to the sample in the brass container. It was made to reach 250ml by adding distilled water. The suspension in the brass container was agitated by a vibrating stirrer for 15 min after which the content was transferred into another 1000 ml measuring cylinder. Distilled water was added to the 1000 ml mark. The diluted content was left to stand for 24hrs to effect the decoagulation of the various powder particles. Manual agitation was done for about a minute and then the cylinder and its contents were placed on a flat bench. A timer was immediately switched on. A hydrometer was then immersed into the cylinder containing the suspension and allowed to float. Hydrometer readings were taken at 30sec, 1, 2 and 4mins, 8 and 24hrs. The sample was washed through 75µm sieve and the contents retained on the sieve were oven-dried at 105°C for 24hrs. The oven dried sample was sieved through some arranged sieve sizes (2.4mm, 1.2mm, 0.4mm, 0.2mm, 150 µm, 75 µm) and the weight retained on each sieve was recorded.

The specific gravity was estimated from a chart which has a relationship with the hydrometer test.

3.3.1.2 Blaine fineness

The Blaine fineness of ordinary Portland cement, clay pozzolana and limestone powders were determined with an air permeability apparatus at the laboratory of Ghana Cement Works (Ghacem) in accordance with ASTM C 204. The apparatus consists of a manometer filled with a non-volatile light grade mineral oil with a cell for holding the samples attached at the top. The apparatus had a calibration constant of 39.813. The cell was filled with 2.715 g of the sample to be analyzed for specific surface area and a filter paper disk placed on top of the bed. The sample was compacted with a plunger after which the cell was placed on top of the manometer.

Air was evacuated from one arm of the manometer until the liquid reached the top mark and allowed to drop to the second mark next to the top. The timer was started and the duration of travel of the liquid from the second to the bottom mark was determined in seconds. The Blaine index was calculated as:

$$S = K\sqrt{t}$$

where

S = Blaine fineness, m^2/kg;

K = calibration constant of the apparatus = 39.813

t = time, s

Fig 3.1 shows the Blaine apparatus

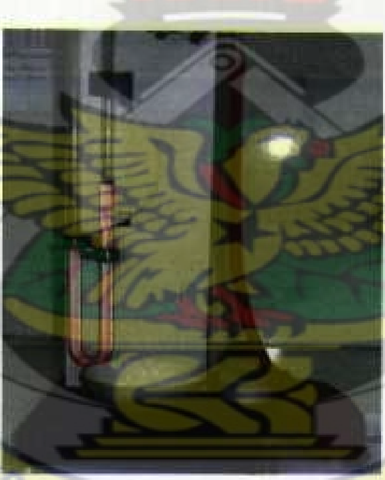

Figure 3.1: Blaine fineness apparatus

3.3.2 Chemical characterization

The chemical analysis was determined using the X-ray fluorescence equipment (spectro X-lab 2000) at the Geological Survey Department in Accra. 4g of the sample (clay pozzolana or limestone powder) was mixed with 0.09g of wax and then milled in a milling machine for 3 minutes to produce a homogeneous mixture. The homogeneous mixture was poured into a disc and placed under a press pellet machine. The pellet machine produced a tab which was placed in a container. The container and its content were fixed in the spectro X-lab. 2000 instrument to determine the chemical composition.

3.3.3 X- ray diffraction analysis clay pozzolana and limestone

The X- ray diffraction patterns of CP and L were determined by X- ray diffractometer in a materials engineering laboratory in Illinois, USA

3.3.4 Microstructure analysis of clay pozzolana and limestone

The microscopical analysis was determined by the use of Scanning electron microscope (JSM-1600 LV) at the department of Zoology, University of Ghana, Legon.

3.3.5 Mechanical properties

3.3.5.1 Compressive strength test

The compressive strength ~~test was~~ determined on mortar mixes in accordance with the BS 4550: part 3. The mortar mix design consisted of both binary and ternary mixtures. Table 3.1 and 3.2 represents the mix designs.

Table 3.1 Binary blend mix containing clay pozzolana (CP) or limestone (L) and ordinary Portland cement (OPC)

Brand name	%CP or L	OPC (%)
CP_0/L_0	0	100
CP_1/L_1	10	90
CP_2/L_2	20	80
CP_3/L_3	25	75
CP_4/L_4	30	70
CP_5/L_5	35	65
CP_6/L_6	40	60

CP/ L; clay pozzolana or limestone

Table 3.2 Ternary blend mix consisting of CP, L and OPC

Brand name	%CP	%L	OPC (%)
T_1	10	20	70
T_2	20	10	70
T_3	15	15	70
T_4	30	20	50

T: Ternary, CP: clay pozzolana, L: limestone, OPC: ordinary Portland cement

All the mortars were prepared with 1:3 binder to sand ratio. The binders consisted of ordinary Portland cement, clay pozzolana and/or limestone. The water to binder ratio for limestone binary blend was maintained at 0.4 whilst for clay pozzolana was between 0.5 and 0.6. The prepared mortar mixes were filled in a 75mm metallic cube moulds. Prior to the mortar filling, the moulds were oiled and arranged on a vibrator which was turned on for 2 minutes to ensure good compaction of the mortar. After casting, the specimens were covered with a wet cloth and stored in a room at a temperature of 24°C for a period of 24 hours and demoulded. The wet cloth helped to control water evaporation from the mortar during the hydration process. The specimens were labeled in conformity with the brand names. The compressive strength was determined after 3, 7, 28 and 90 days of wet curing. The strength recorded was for an average of 3 specimens. Figure 3.2 shows the compressive strength testing machine used to determine the strength values at the Civil engineering laboratory at K.N.U.S.T in Kumasi.

Figure 3.2 Compressive strength testing machine

3.3.5.2 Water demand or normal consistency

The water demand was determined as specified by EN 196-3. This specification employs the use of the Vicat apparatus. Fig 3.3 shows a picture of the Vicat apparatus. Figs 3.4, 3.5 and 3.6 show the plunger, needle with ring and the Vicat needle used for the test. Cement pastes were prepared using 10%, 20%, 25%, 30%, 35% and 40% clay pozzolana and limestone replacement levels respectively as binary blended mixtures at room temperature. Table 3.4 as shown above also shows the mix design for the ternary paste formulation. The plunger attached to the apparatus was adjusted in reference to the base plate so as to make the pointer on the scale to read zero.

Figure 3.3: Vicat apparatus

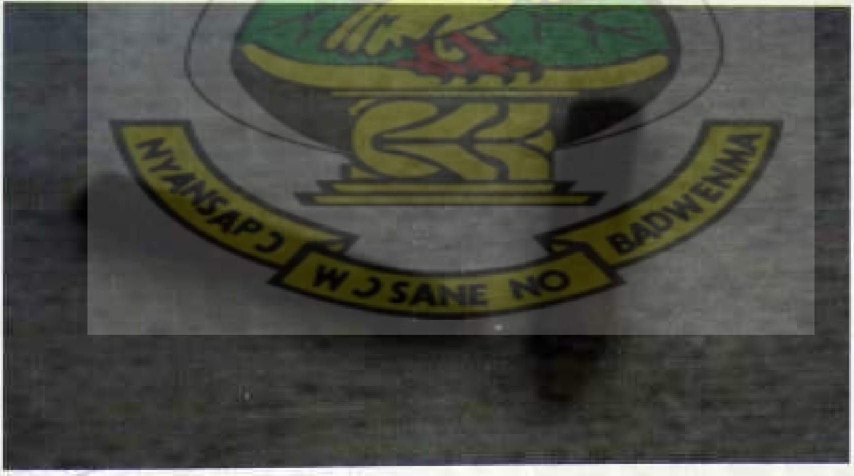

Figure 3.4: Plunger

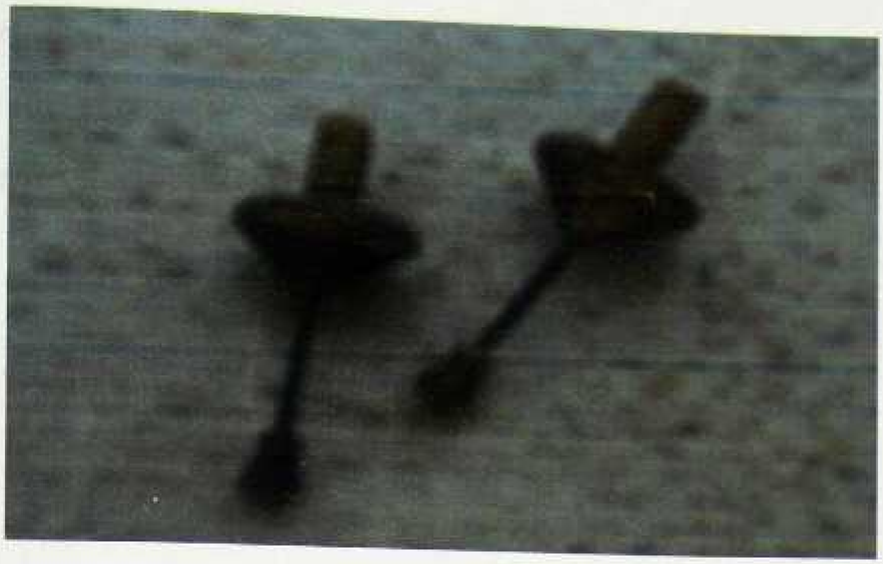

Figure 3.5 Needle with ring

Figure 3.6 Vicat needle

The Vicat mould was filled with the paste which had previously been placed on a lightly greased plain glass plate. The apparatus was filled to excess without compaction. The excess paste was removed by a gentle sawing with the trowel so that the paste attained an upper smooth surface. The Vicat mould together with the base plate was positioned centrally under the Vicat apparatus where the plunger had been raised to a stand-by position. The plunger was then lowered gently until it came into contact with the paste at the surface. The water demand was determined after making trial mixes of the paste giving a reading of 6±2 on the scale. The reading indicates the distance between the bottom of the base plate and the plunger.

3.3.5.3 Setting times

3.3.5.3.1 Initial setting time

The initial setting time was determined as specified by EN 196-3. Cement paste of standard consistency was prepared. The Vicat plunger was removed from its position and replaced by the Vicat needle as shown in Fig 3.4. The needle was adjusted with reference to the base plate so as to make the pointer read zero on the scale. The paste of standard consistency was filled into an already greased mould on the base plate. The needle which had been raised to a stand-by position was lowered to come into contact with the smooth-cut upper surface of the paste. The moving part of the needle was released to make penetration through the paste. The initial setting time was recorded at the point when the scale recorded 6±3 from the zero point. This reading shows the distance between the base plate and the end of the needle.

3.3.5.3.2 Final setting time

The final setting time was also determined in accordance with EN 196-3. The vicat needle was removed and ~~replaced by~~ the needle with a ring as shown in Fig 3.6. The filled paste and mould were inverted so that the test for the final setting time was made on the face originally in contact with the base plate. The specimen was stored under a damp cloth for about 60 seconds. After about 5 seconds from the initial time of 60 seconds, the base plate and the mould were positioned under the needle. The movable part of the needle was released to make contact with the specimen surface. The final setting time was recorded at a point the ring attachment to the needle failed to make an impression on the specimen surface.

3.3.6 Durability test

3.3.6.1 Mortar resistance against 2% Na_2SO_4

Mortar cubes of 1:3 binder- to- sand ratio were prepared and cured by immersion in potable water for 28 days. Water- to- binder ratio used for the ordinary Portland cement and clay pozzolana mortar mix ranged from 0.5 to 0.6. The ordinary Portland cement, limestone mortar and the ternary mortar mixes all used water- to- binder ratio of 0.5. After 28 days of curing the mortar cubes were oven dried and their weight taken before being exposed to 2% Na_2SO_4 solution for 90 days. After 90 days the mortar cubes were removed, reweighed and tested using visual observation and compressive strength test. The compressive strength was compared with mortar cubes cured throughout under similar wet conditions for the same number of days.

3.3.6.2 Preparation of 2% Na_2SO_4

20 g of sodium sulphate anhydrous (Na_2SO_4) was weighed into a beaker and dissolved with about 100 ml of distilled water. The dissolved solution was transferred into a 1000 ml volumetric flask and diluted with distilled water to the mark. The solution was corked and shaken for homogeneity.

CHAPTER FOUR

4.1 RESULTS AND DISCUSSIONS

4.2 Physical characterization

Table 4.1 shows the results of the physical test conducted on the Ordinary Portland Cement (OPC), Clay Pozzolana (CP) and Limestone (L).

The specific gravity of CP and L are comparable, 2.58 and 2.56 respectively while OPC had a higher specific gravity of 3.14. Blaine fineness index for limestone was the highest, 420 m^2/kg followed by CP, 410m^2/kg and lastly OPC having 338m^2/kg. Limestone having a higher Blaine value indicates a higher surface area whereas OPC Blaine value indicates a lower surface area. OPC had the least mean particle size, 4μm whilst CP and L had close range mean particle values being 30 and 32 μm respectively. Table 4.1 also shows that the percentage of OPC, CP and L that passed 75 μm sieve size were 92, 99.6 and 98% respectively. This indicates that virtually almost all the powder samples were retained under 75 μm sieve size.

Table 4.1 Physical properties of OPC, Clay pozzolana and limestone

Property	OPC	CP	L
Sp gravity	3.14	2.58	2.56
Blaine fineness(m^2/kg)	338	410	420
Mean particle size(μm)	4	30	32
% passing 75(μm)	92	99.6	98

Figure 4.1 represents the results of the particle size analysis determined on OPC, CP and L. The data shows that OPC, CP and L fall in the range of 0.0015-2.25mm, 0.0017-0.135mm and 0.0033-10.00mm respectively. Clay pozzolana and limestone show a uniformly graded sample whilst OPC indicated a well graded sample. Clay pozzolana contained more fine particles than limestone and cement powder. Figure 4.1 represents results of the sedimentation test used to analyze the particles sizes of OPC, CP and L.

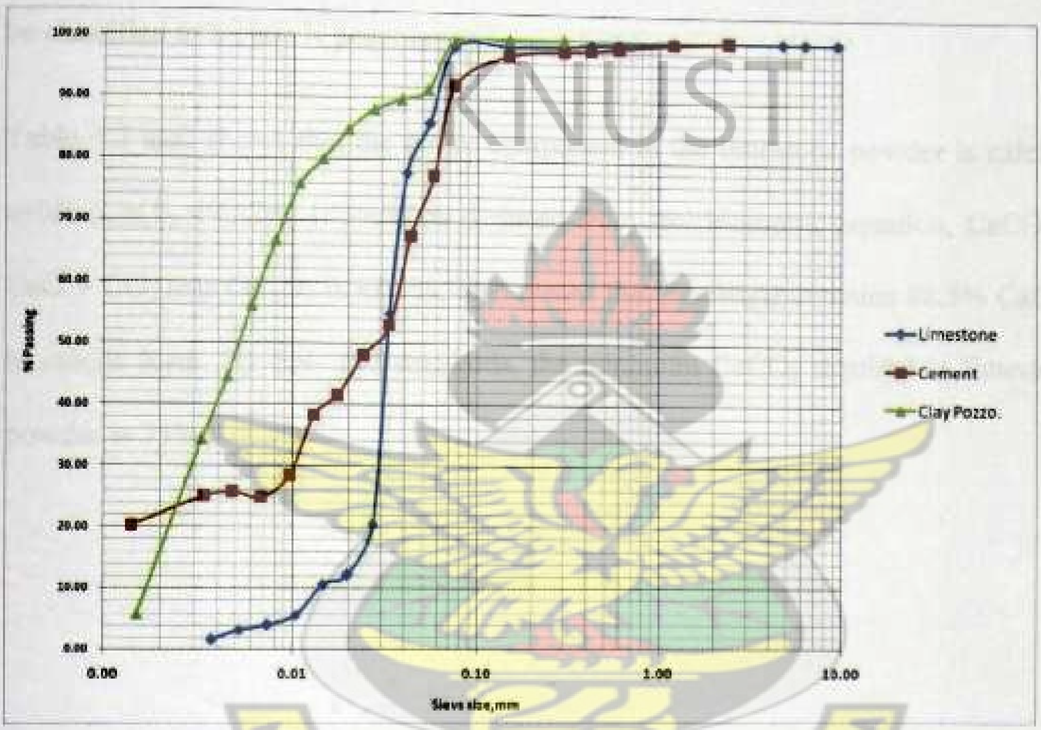

Figure 4.1: Particle size analysis of OPC, CP and L

4.3 Chemical characterization

Table 4.2 shows the results of the chemical analysis done on clay pozzolana (CP) and limestone (L). Results of ~~the chemical~~ and mineralogical composition of OPC were obtained from Ghana Cement Works (Ghacem) (Ordinary Portland cement report, 2007)

It is indicated in Table 4.2 that the major chemical composition of OPC are CaO, 63.03%, followed by SiO_2, 19.7% and Fe_2O_3, 3.16. The main compounds in OPC are C_3S, 59.6%, C_2S, 12.6%, C_3A, 7.86 and C_4AF, 9.49%.

Clay pozzolana (CP) is composed of SiO_2, Al_2O_3 and Fe_2O_3 which together constitute 81.24%, 0.14% is SO_3 and 10% LOI. By ASTM standards class N pozzolana is composed of a minimum sum of 70% comprising of SiO_2, Al_2O_3 and Fe_2O_3, maximum of 4% SO_3 and a maximum of 12% LOI. This implies that CP can be classified as a class N pozzolana.

Table 4.2 also shows that the major component in the limestone powder is calcium oxide (CaO), 49.57%. It could be deduced from stoichiometric equation, $CaCO_3 \rightarrow CaO + CO_2$ that $CaCO_3$ is 88.5%. This means that limestone contains 88.5% $CaCO_3$ in calcite form. By EN- 197 standards, the minimum $CaCO_3$ required in limestone powder is 75%.

Table 4.2: Chemical and mineralogical composition of OPC, CP and L

Compound (%)	OPC	CP	L
SiO_2	19.7	61.89	17.65
Al_2O_3	5	13.51	3.45
Fe_2O_3	3.16	5.84	1.56
CaO	63.03	0.21	49.57
MgO	1.75	1.74	2.11
K_2O	0.16	1.07	0.78
Na_2O	0.2	0.14	0.3
SO_3	2.8	0.14	0.3
LOI	2.58	10	23.43
$SiO_2+Al_2O_3+Fe_2O_3$	–	81.23	–
C_3S	59.6	–	–
C_2S	12.6	–	–
C_3A	7.86	–	–
C_4AF	9.49	–	–

4.4 X- ray diffraction analysis of clay pozzolana and limestone

Figure 4.2 shows the X ray diffraction pattern of Mankranso Clay Pozzolana (CP). According to Figure 4.2, the diffraction analysis shows the presence of kaolinite, quartz, calcite and goethite. The diffraction peaks relative to kaolinite, calcite and goethite was less pronounce whereas diffraction peaks relative to quartz showed a pronounce diffuse peak between 20 and 30°.

The results show that kaolinite present in the raw clay is transformed into glassy phase (quartz) through calcinations of raw clay, potentially reactive with portlandite ($Ca(OH)_2$) released when Portland cement hydrates. Also, the presence of quartz between 20 and 30° indicate the amorphous nature of the clay pozzolana.

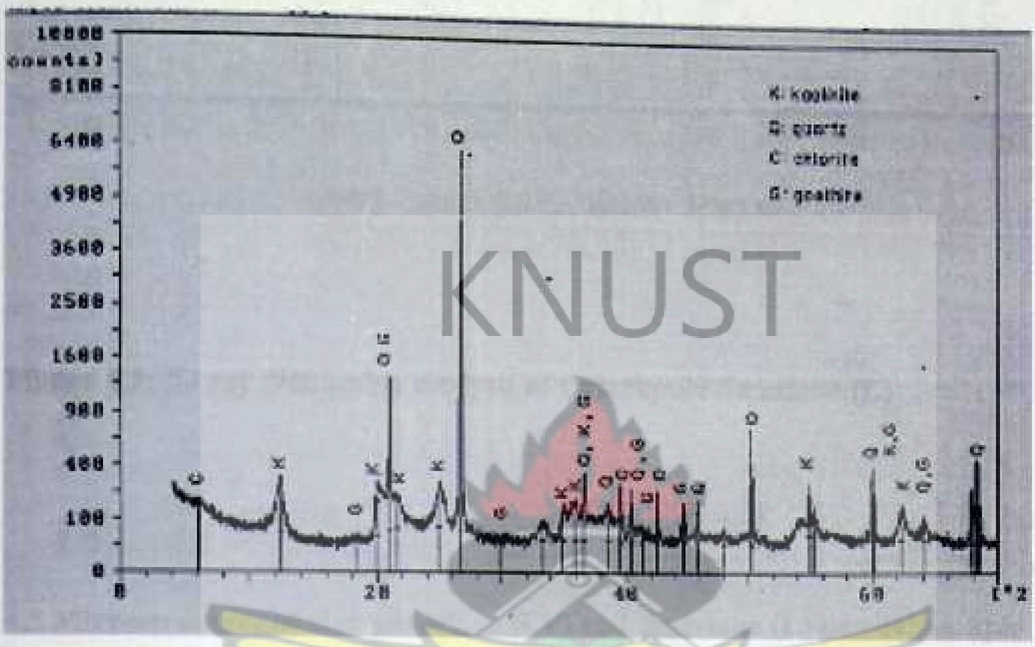

Figure 4.2: X- ray diffraction analysis of Mankranso clay pozzolana (CP)

The X- ray diffraction analysis of Orterkpolu limestone (L) is shown in Figure 4.3. The diffraction results show three nearby pits at different locations. The results confirm the presence of calcite ($CaCO_3$), together with calcareous dolomite ($CaMg(CO_3)_2$) and minor constituent of silica (SiO_2). From the diffraction results, it could be confirmed that there was no undesirable argillaceous component present in the limestone powder.

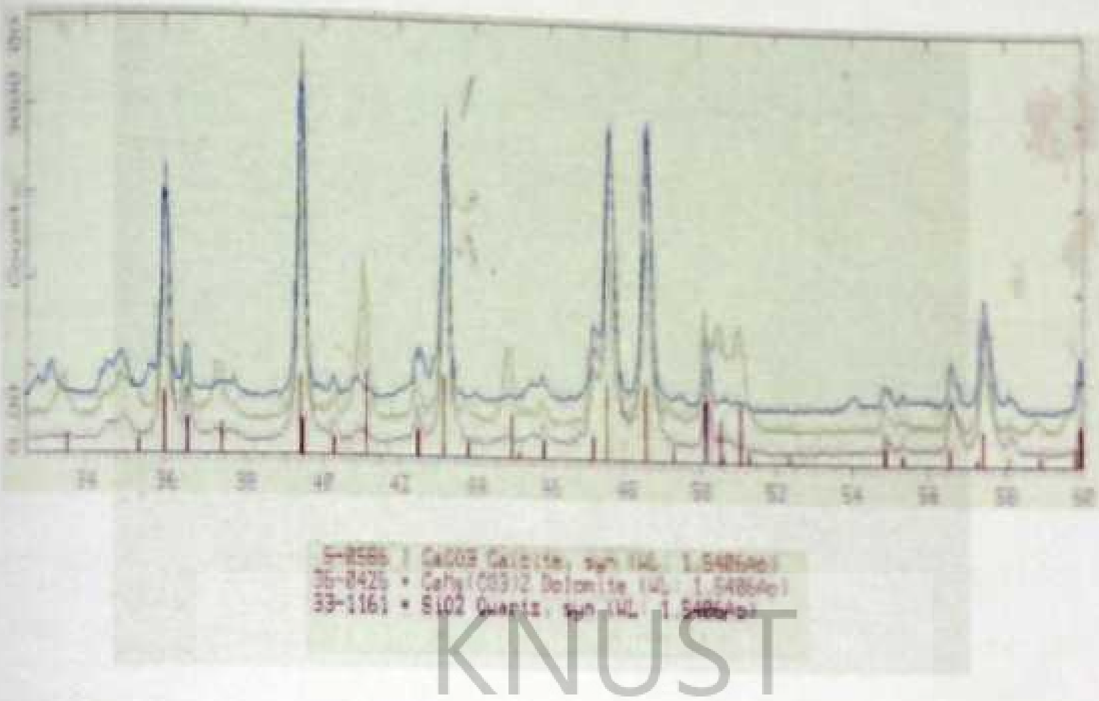

Figure 4.3: X- ray diffraction analysis of Orterkpolu limestone (L)

4.5 Microstructure of clay pozzolana (CP) and limestone (L) powder sample

Figures 4.4 and 4.5 represent the microstructure of clay pozzolana (CP) and limestone (L). Both powder specimen shows that their shapes are irregular; however limestone powder sample shows more irregular shapes than clay pozzolana powder.

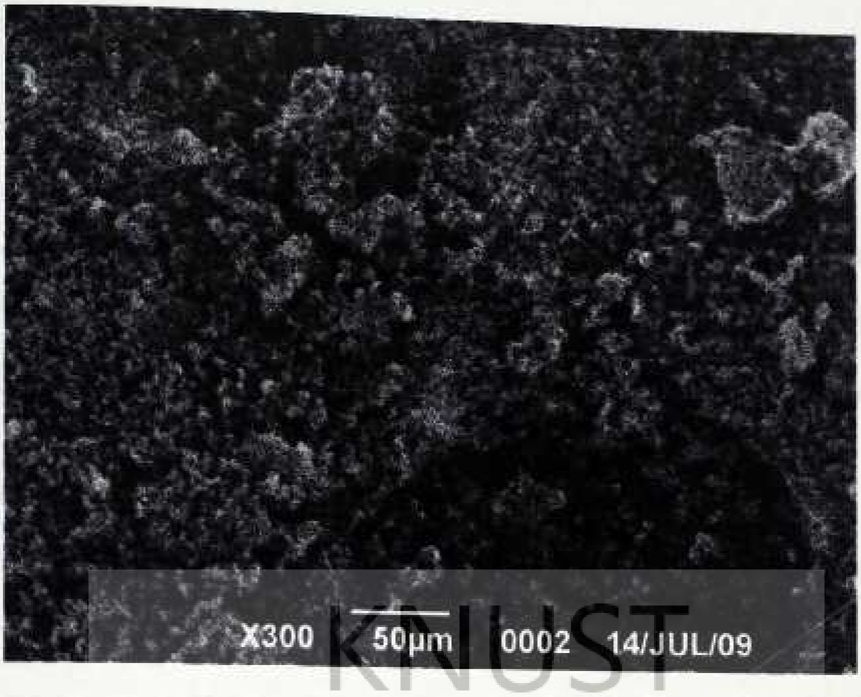

Figure 4.4 Microstructure of clay pozzolana (CP) powder specimen

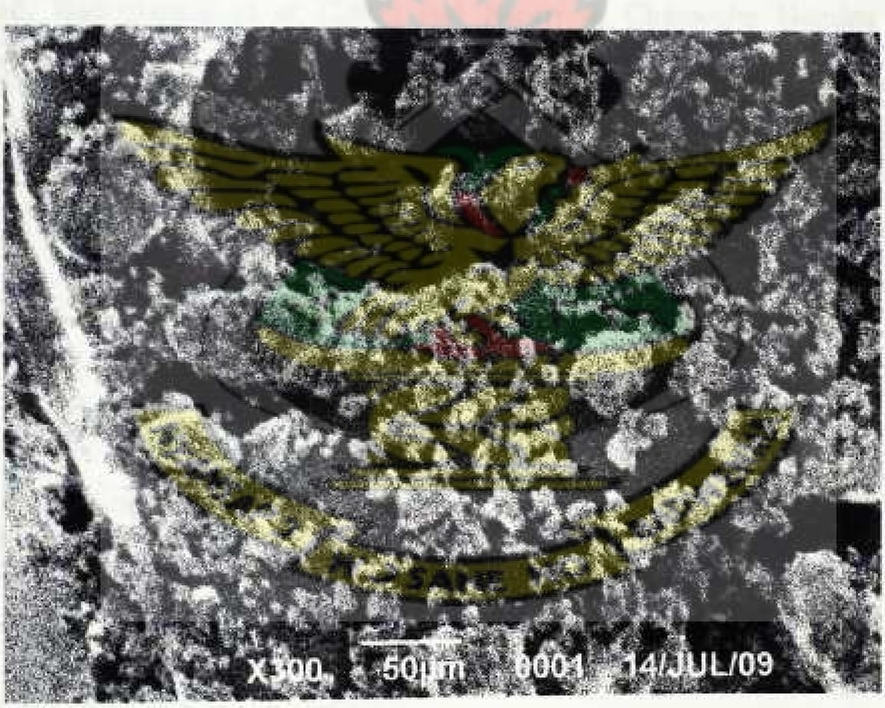

Figure 4.5 Microstructure of limestone (L) powder specimen

4.6 Mechanical properties

4.6.1 Water demand

Figures 4.6 to 4.8 show graphical results of water demand test of binary paste consisting of either clay pozzolana (CP) or limestone (L) and ordinary Portland cement (OPC) and ternary paste which comprises of CP and L together with OPC.

The graphical results from figure 4.6 which represent water demand of blended pozzolana paste indicate that the water demand of clay pozzolana (CP) incorporation at 10, 20, 25, 30, 35 and 40% was higher, between 10.7% and 42.9% more than the plain cement paste which is deduced from the graph. Figure 4.6 also shows a progressive increase in the water demand as CP content in the blended paste increased. Badogiannis *et al* (2005) and Naceri & Chikouche Hamina (2009) reported similar trend on their investigations on pozzolana and cement mixture paste. According to Samet *et al* (2007), the high water demand of blended clay pozzolana paste than OPC paste is due to the more porous nature of clay pozzolana.

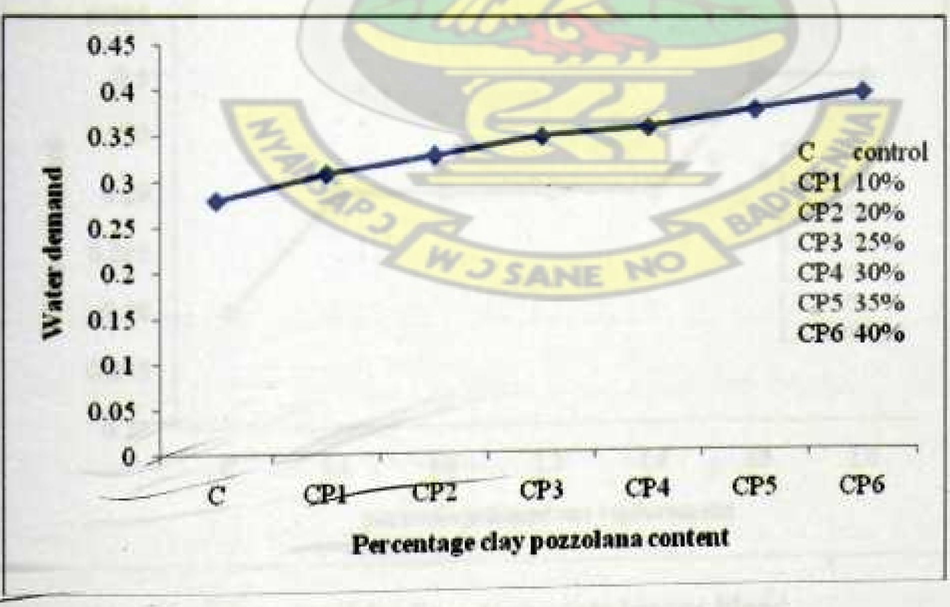

Figure 4.6 Water demand for pozzolana paste binary blend

The results of limestone (L) blended paste is shown in Figure 4.7. From the figure, it is seen that the inclusion of limestone powder at 10%, 25%, 30%, 35%, and 40% replacement of ordinary portland cement (OPC) required higher water demand, estimated between 3.6% and 7% more than the pure cement paste from the graph. Water demand at L1 (10%), L2 (20%), L3(25%) and L4(30%) remained steady at 0.29. Beyond L4 (30%), that is at L5 (35%), water demand increased to 0.3 which was the highest. It remained steady at this highest point of 0.3 up to L6 (40%).

Similar water demand results were obtained by Helal (2002). He explained the reason for the high water demand of limestone incoporated paste compared with OPC paste as due to the higher absorption capability of limestone powder. L5 (35%) and L6 (40%) which indicated the highest water demand show that the blended cement paste contained more finer particles and therefore a higher surface area (Rao Appa, 2003).

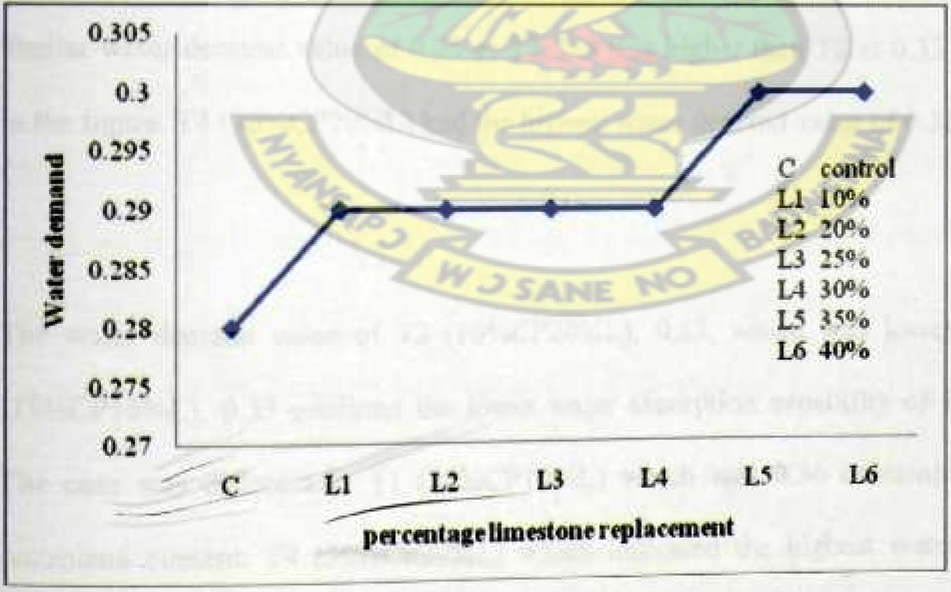

Figure 4.7 Water demand for limestone paste binary blend

From Figure 4.6 and 4.7 it is seen obviously that the binary paste showed a higher water demand capability than the pure cement paste, however, comparing the two that is CP and L pastes, clay pozzolana (CP) incorporated paste indicates a higher water demand than the limestone (L) incorporated paste.

Figure 4.8 shows the result of ternary (T) paste which involves clay pozzolana (CP), limestone (L) and ordinary Portland cement (OPC). The total weight percent of CP and L in T1, T2 and T3 paste is 30% whereas for T4 paste is 50%. From the results, it is seen that, the inclusion of the two minerals, CP and L labeled as T1(20%CP10%L), T2(10%CP20%L), T3(15%CP15%L) and T4 (30%CP20%L) attained a high water demand, estimated between 17.6% and 35.7% more than ordinary Portland cement paste (C) as illustrated in Figure 4.8. T1 (20%CP10%L) which contains more clay pozzolana (CP) and lower limestone (L) content than T2 (10%CP20%L) indicated a 9% increase in water demand than T2 as deduced from the graph. T3 (15%CP15%L) which contains equal weight percent of CP and L had similar water demand value of 0.35 as T1, but was higher than T2 at 0.33 as shown in the figure. T4 (30%CP20%L) had the highest water demand value of 0.38.

The water demand value of T2 (10%CP20%L), 0.33, which was lower than T3 (15%CP15%L), 0.35 confirms the lower water absorption capability of limestone. The case was different in T1 (20%CP10%L) which was 0.36 containing a high pozzolana content. T4 (30%CP20%L) which indicated the highest water demand could be due to the high clay pozzolana content present in the ternary mixture which shows a high porous nature.

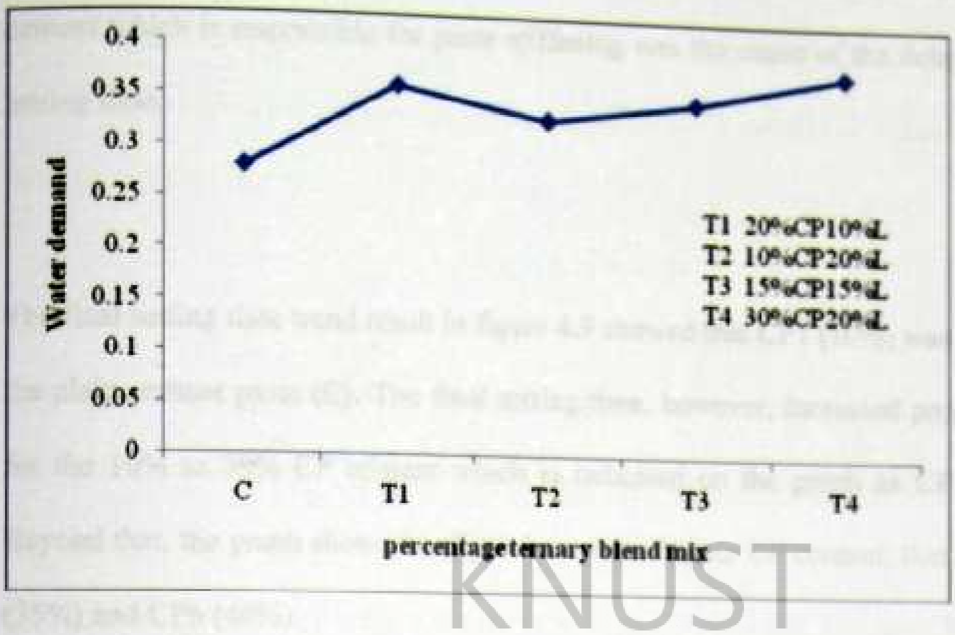

Figure 4.8 Water demand for ternary blended paste

4.6.2 Setting time

Figures 4.9 to 4.11 give the graphical results of setting times, both initial and final, of binary paste involving clay pozzolana (CP) or limestone (L), and ternary paste consisting of CP and L with ordinary Portland cement (OPC) as the remainder.

Figure 4.9 shows results of the initial and final setting times of CP paste. From the figure, the initial setting times of CP1 (10%), CP2 (20%) and CP3 (25%) were similar to the pure cement paste (C). Beyond 25% of CP content in the cement paste, there was a progressive increase in the initial setting time for 30%, 35% and 40% of pozzolana content labeled on the graph as CP4, CP5 and CP6.

The results of the initial setting time trend in figure 4.9 shows that CP content between 10 and 25% behaved as inert fillers whereas at higher weight percent of CP content in cement paste that is between 30% and 40 %, the decrease in Portland cement which is responsible for paste stiffening was the cause of the delayed initial setting time.

The final setting time trend result in figure 4.9 showed that CP1 (10%) was similar to the plain cement paste (C). The final setting time, however, increased progressively for the 10% to 30% CP content which is indicated on the graph as CP1 to CP4. Beyond that, the graph showed a slight decrease at higher CP content, that is, at CP5 (35%) and CP6 (40%).

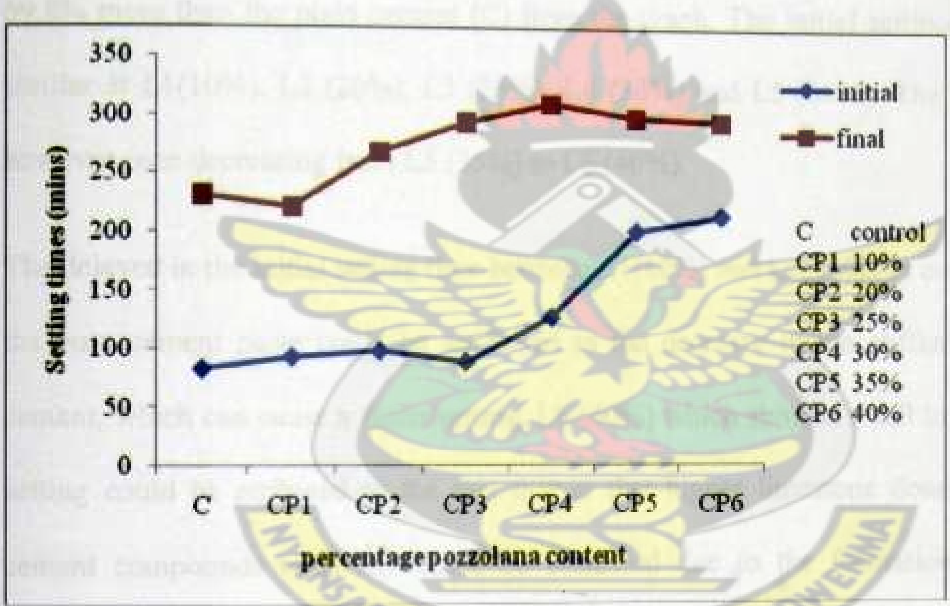

Figure 4.9: Setting times of Clay pozzolana and OPC paste

The results as shown in figure 4.9 indicate that 10% of CP content in cement paste behaved as an inert filler even at the final setting time; however, between 10% and 30% of clay pozzolana content, the final setting times were retarded due to pozzolanic effect. The slight decrease in the final setting time indicated for CP5

(35%) and CP6 (40%) as shown in the graph, Figure 4.9 could mean that additional binder phase was produced. Brooks *et al* (2000) explained that, when a pozzolana is added to cement at certain dosage, extra binder phase is produced which speeds up the final setting time

Figure 4.10 shows the setting times results of blended limestone and cement paste. It could be seen from the graph that, the initial setting time of the blended paste containing 10%, 20%, 25%, 30%, 35% and 40% limestone powder labelled as L1, L2, L3, L4, L5 and L6 respectively were higher, estimated between 27.7% and 69.8% more than the plain cement (C) from the graph. The initial setting time was similar at L1(10%), L2 (20%), L3 (25%), L4 (30%) and L5 (35%). The trend was however seen decreasing from L5 (35%) to L6 (40%).

The delayed in the initial setting time between L1(10%) and L6(40%) as compared to the pure cement paste could be attributed to the decrease in the stiffening agent, cement, which can cause a faster setting. L6 (40%) which showed a fall in the initial setting could be atributed to the fact that at that higher limestone dosage (40%), cement compounds reactivity could be enhanced due to the formation of more $Ca(OH)_2$.

The final setting time as shown in figure 4.10 was reduced at L1 (10%), L2 (20%), L3(25%), L4 (30%) and L5 (35%), estimated between 12.6% and 25.5% less than the ~~plain~~ cement paste (C) from the graph. A similar final setting time results was obtained by Helal (2002). He explained that, the decrease in the setting time was due to the formation of increased amounts of calcium carboaluminate hydrates, which have a high rate of formation at early ages of the hydration process. The explanation offered by Heikal (2000) and Irassar *et al* (2000) to this particular trend is that limestone addition enhances the formation of $Ca(OH)_2$ at the early ages because it provides nucleating sites for its growth. At L6 (40%), the final setting time occured at 232 minutes almost the same as the plain cement paste which occured at 231 minutes. This trend could mean that limestone filler at that dosage (40%) caused a dilution in the cement paste matrix and as a result caused a delay final setting time.

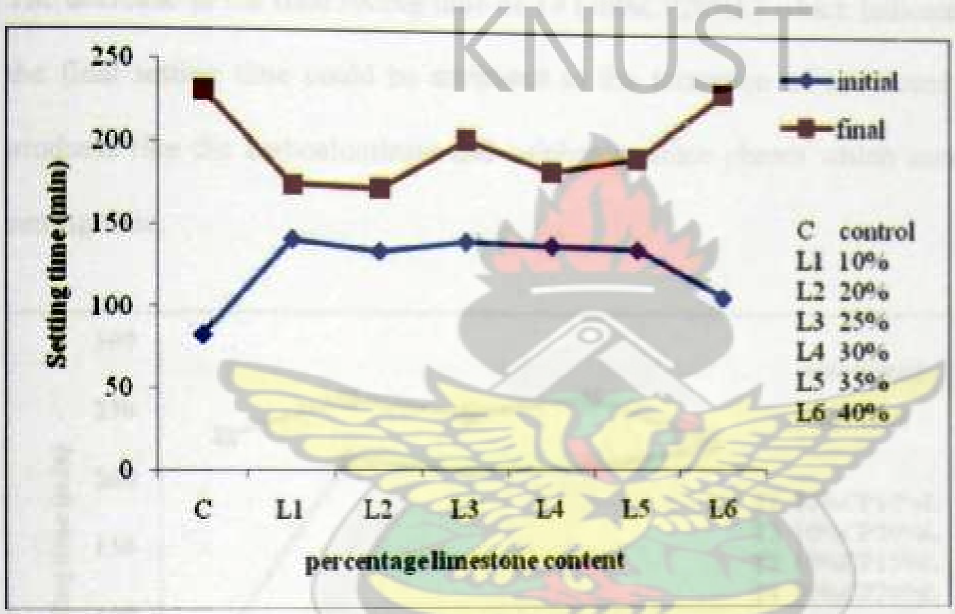

Figure 4.10: Setting times of limestone and OPC paste

Figure 4.11 shows the graphical trend of ternary (T) blended paste. It could be seen that the initial setting time of the blended cement paste containing T1 (20%CP10%L), T2 (10%CP20%L), T3 (15%CP15%L) and T4 (30%CP20%L) were higher, estimated from the graph to be between 147% and 167% more than the pure cement paste (C). The initial setting time trend remained almost steady at T1(20%CP10%L), T2(10%CP20%L), T3(15%CP15%L) and T4(30%CP20%L).

The reason for the high delay of initial setting time at T1, T2, T3 and T4 as compared to ordinary portland cement paste (C) could be due to the effect of admixtures, which delay the reaction between the cement and mixing water.

The final setting time trend as indicated in figure 4.11 shows that the plain cement and the ternary paste, T1 (20%CP10%L), T2 (10%CP20%L) and T3 (15%CP15%L) were similar. The trend however showed a slight decrease in the final setting time at T4 (30%CP20%L).

The decrease in the final setting time of T4 (30%CP20%L) which indicated a fall in the final setting time could be attributed to the formation of additional hydration products like the carboaluminate and sulphoaluminate phases which accelerate the setting time.

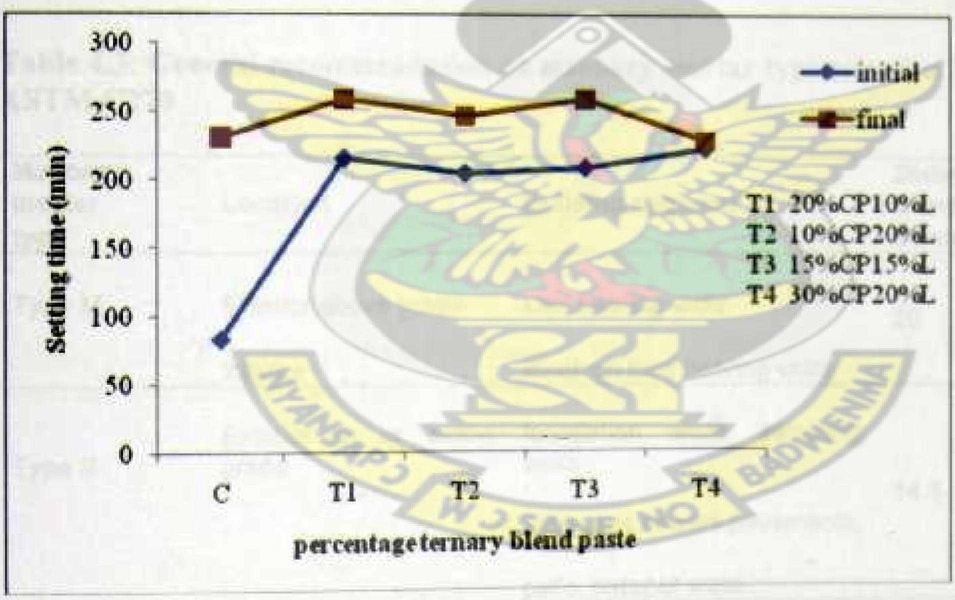

Figure 4.11: Setting times of ternary blend paste

4.6.3 Compressive strength

4.6.3.1 Masonry mortar class based on compressive strength

Figures 4.12 to 4.14 show the 28 days compressive strength results of binary mortar mixture containing clay pozzolana (CP) or limestone (L), and of ternary (T) mortar mixture that contained CP and L. It is indicated from figure 4.12 to 4.14 that the minimum strength requirement for masonry mortar classified as type M and S are 20.0MPa and 14.8MPa respectively according to ASTM standards. It is also in accordance with ASTM C270 standards that type M mortars are used for above grade exterior load bearing walls and interior load and non load bearing walls, whereas type S mortars are suitable for foundation walls, retaining walls, manholes, sewers, pavements, patio and parapet walls (see table 4.3).

Table 4.3: General recommendation on masonry mortar type selection by ASTM C270

Masonry mortar type	Location	Building segment	28days compressive Strength (MPa)
Type M	Exterior above grade	load bearing walls	20
	Interior	load/non load bearing walls	
Type S	Exterior at or below grade	foundation walls, retaining walls manholes,sewers,pavements, patio, parapet walls	14.5

From Figure 4.12 which represents the masonry mortar strength results of CP and OPC mixture, it could be seen that the plain mortar (C), CP1 (10%) and CP2 (20%) had strength values of 26.0 MPa, 21.7 MPa and 20.3 MPa respectively. These values are higher than ASTM type M and S mortars. The mortar strength values for CP3 (25%), CP4 (30%), CP5 (35%) and CP6 (40%) were 18.5 MPa, 18.0 MPa, 17.9 MPa and 16.2 MPa respectively which are higher than type S mortar strength of 14.8 MPa but less than that of type M mortar.

The results from figure 4.12 shows that mortar that contains 10% and 20% of CP content was suitable to produce a type M mortar whereas clay pozzolana contents between 25% and 40% were on the other hand suitable for a type S mortar.

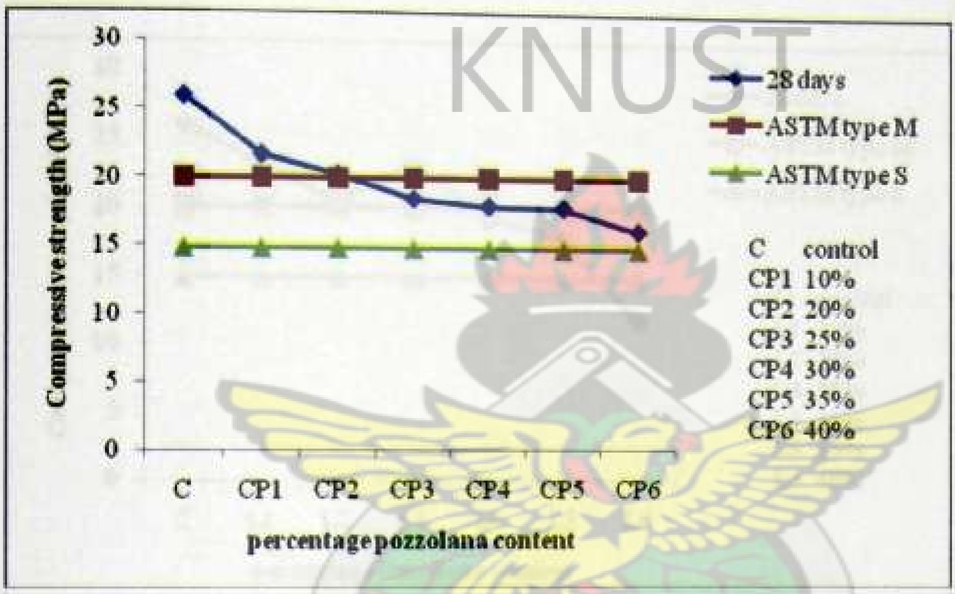

Figure 4.12: 28-days Compressive strength of OPC-CP masonry mortar compared to ASTM standards

Figure 4.13 shows masonry mortar strength results of limestone (L) and ordinary portland cement (OPC) mixture. Compressive strength values of plain cement (C), L1 (10%), L2 (20%) and ~~L3 (25%)~~ were 26.0 MPa, 23.1 MPa, 20.4 MPa and 23.2 MPa respectively, higher than 20.0 MPa required for a type M mortar. L4 (30%) and L5 (35%) were 19.2 MPa and 17.8 MPa respectively were higher than the minimum strength required for type S mortar of 14.8MPa. L6 (40%) had a value of 11.7 MPa which is below the type S mortar requirement.

The results suggest that 10% and 25% of limestone contents (L) in cement mortar are more appropriate for a type M mortar whilst those from 30% to 35% are suitable for a type S mortar. Limestone content of 40% in masonry mortar is not suitable for either type M or S mortar.

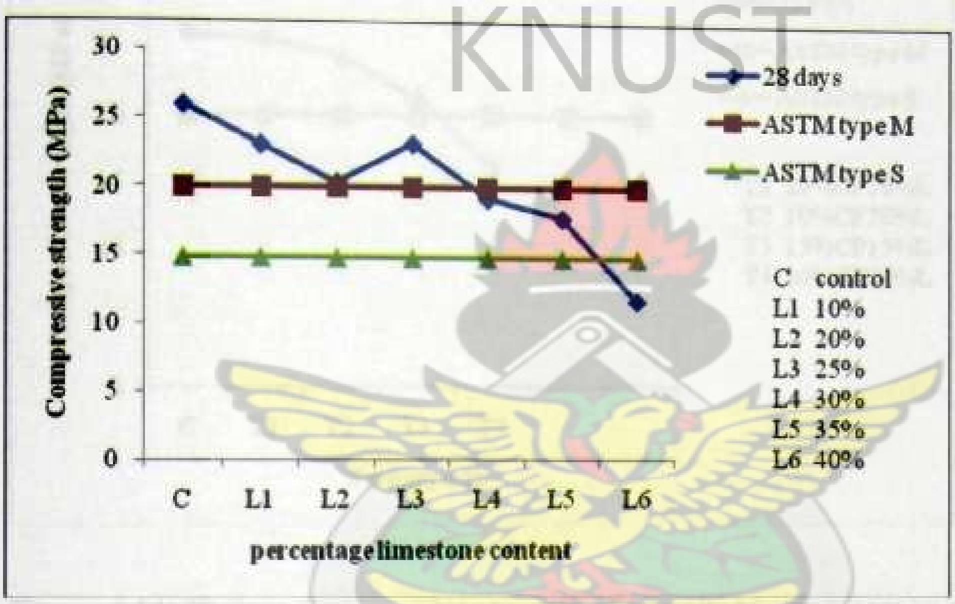

Figure 4.13: 28-days Compressive strength of OPC-L masonry mortar blend compared to ASTM standards

Figure 4.14 shows the masonry mortar strength results of ternary mixture which consist of OPC, CP and L. From the figure, the compressive strength values for plain cement ~~(C),~~ T1 (20%CP~~10%L), T2~~ (10%CP20%L) and T3 (15%CP15%L) were 26.0 MPa, 25.6 MPa and 21.3 MPa respectively and higher than the minimum strength of 20 MPa required for type M mortar. The compressive strength value for T4

(30%CP20%L) was 16.3 MPa, which is higher than the type S mortar strength of 14.8 MPa.

It can be inferred from the results that T1 (20%CP10%L), T2 (10%CP20%L) and T3 (15%CP15%L) best suit a type M mortar whereas T4 (30%CP20%L) is more appropriate for type S mortar.

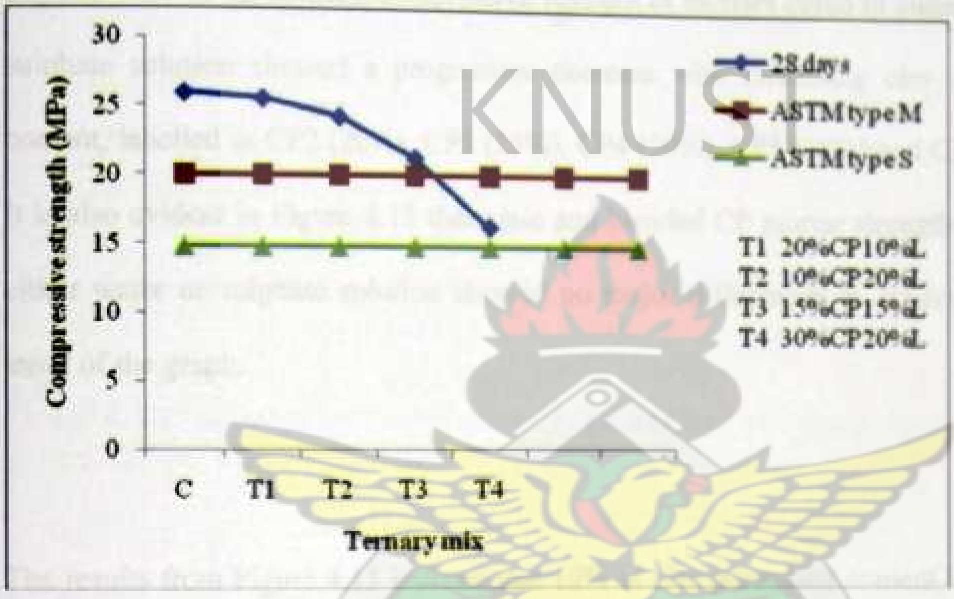

Figure 4.14: 28-days Compressive strength of ternary blend masonry mortar compared to ASTM standards

4.7 Aspect of durability analysis of mortar for masonry.

4.7.1 Mortar resistance to sulphate attack

Figures 4.15 to 4.17 represent the compressive strength of plain and blended mortars cured in water for control, and in sodium sulphate solution for a period of 90 days. The results show that the mortar strength for plain mortar mix (C) obtained when cured in water was 30.9MPa. In sulphate solution, the compressive strength was 27.9

MPa which indicate that the compressive strength of mortar cured in water was about 10% higher than mortar cured in sulphate solution.

Figure 4.15 represents results of clay pozzolana (CP) and cement mortar mixes. It is observed that the compressive strengths of CP1 (10%) cured in water and sodium sulphate solution were 34.3 and 34.1 MPa respectively, recorded as the highest. Beyond 10% of CP content, compressive strength of mortars cured in either water or sulphate solution showed a progressive decrease with increasing clay pozzolana content, labelled as CP2 (20%), CP3 (25%), CP4 (30%), CP5 (35%) and CP6 (40%). It is also evident in Figure 4.15 that plain and blended CP mortar strengths cured in either water or sulphate solution showed no major differences as observed in the trend of the graph.

The results from Figure 4.15 indicate that 10% of clay pozzolana content in cement mortar showed the highest ressistance against the ingress of water and sodium sulphate solution since it had the highest strength. Similar results were obtained by Singh and Garg (2006). They attributed this trend of results to the formation of higher amount of calcium silicate hydrate (CSH) and other hydration products in OPC-CP mix which happen as a result of higher rate of reation between amorphous silica and alumina from CP with the lime that is released from cement.

The progressive decrease in strength with increasing clay pozzolana content was explained by O′ Farrel *et al* (2006). He attributed this trend to the dilution effect of pozzolana addition in cement mortars. The result also suggest that for clay pozzolana content between 10 and 40% in mortar, sulphate attack is of minimal effect.

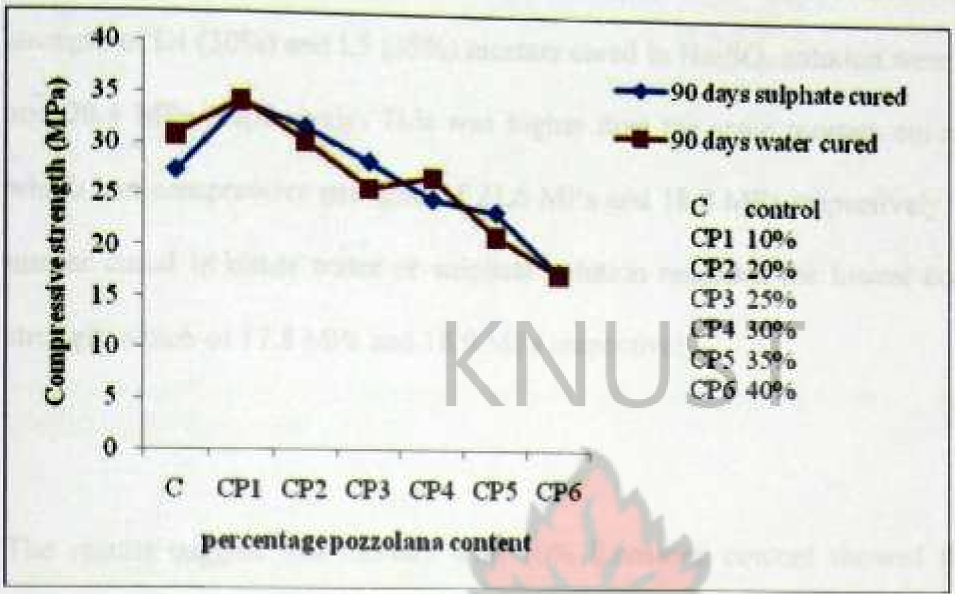

Figure 4.15: Compressive strength of Clay pozzolana and cement mortars cured in Na_2SO_4 and water for 90 days

Figure 4.16 gives the compressive strength of limestone (L) and portland cement mortar mixture cured in water and sodium sulphate solution. The results show that at L1 (10%), the compressive strength obtained when cured in water and sulphate solutions were 36.8 MPa and 34.5 MPa respectively, being the highest among the other mortars, L2 (20%), L3 (25%), L4 (30%), L5(35%) and L6 (40%). Beyond L1 (10%), the graph showed a progressive decrease in strength with increasing limestone content (20%-40%) when cured either in water or sulphate.

The graph shows that the compressive strengths for L1 (10%), L2 (20%) and L3 (25%) cured in Na_2SO_4 solution were 34.5 MPa, 29.3 MPa and 24.0 MPa, slightly lower than mortars cured in water which had compressive strengths of 36.0 MPa, 31.0 MPa and 26.0 MPa respectively. The graph also shows that compressive strength of L4 (30%) and L5 (35%) mortars cured in Na_2SO_4 solution were 26.0 MPa and 20.4 MPa respectively. This was higher than the same mortars cured in water which had compressive strengths of 21.6 MPa and 18.0 MPa respectively. L6 (40%) mortar cured in either water or sulphate solution recorded the lowest compressive strength which of 17.8 MPa and 18.9 MPa respectively.

The results suggest that mortars with 10% limestone content showed the highest resistance against water and sulphate solutions. This is essentially due to the acceleration effect of limestone filler related to the formation of calcium carboaluminate hydrate, which may contributed to the overall increase in the the rate of hydration. Also, the carboaluminate formation is likely to make the mortar structure compact (Baron and Douvre, 1987). Limestone contents at L5 (35%) and L6 (40%) which gave a good resistance in sulphate solution than in pure water can be attributed to the dense nature of newly formed calcium carboaluminate hydrate (3CaO. Al_2O_3. $CaCO_3$. $11H_20$) that filled the pore structure of cement paste resulting in a strength gain (Guemmadi *et al*, 2008).

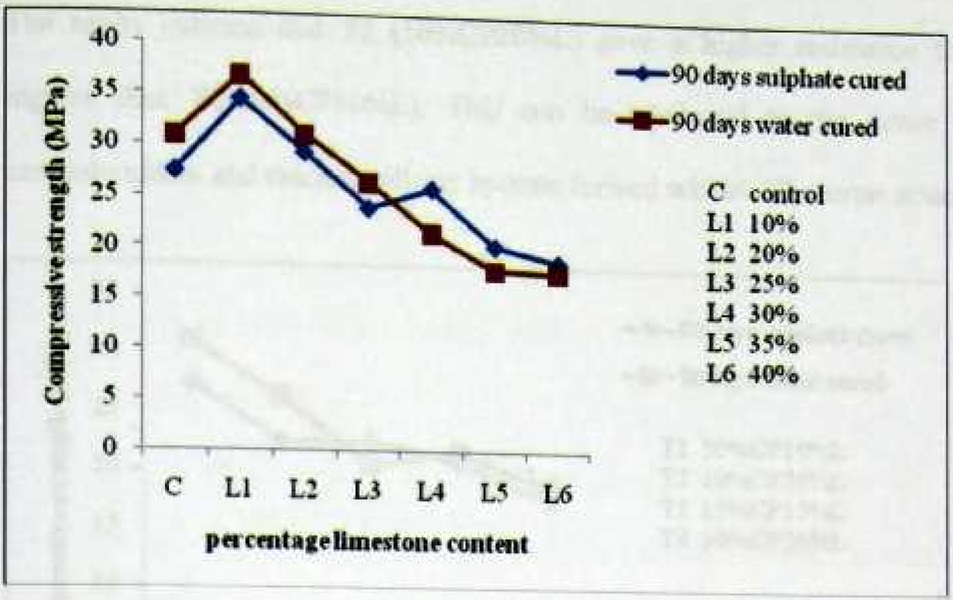

Figure 4.16: Compressive strength of limestone and cement mortars cured in Na_2SO_4 and water for 90 days.

The results for the ternary mixture is given in Figure 4.17. It can be seen that the compressive strength of T1(20%CP10%L) cured in water was 26.2 MPa. In Na_2SO_4 solution, the compressive strength of T1(20%CP10%L) was 22.3 MPa which represented a 14.9 % decrease compared with mortar cured in water. The compressive strengths of T2 (10%CP20%L) cured in water and sulphate solution were 22.5 MPa and 20.4 MPa respectively. This represents a 10% gain in strength of the mortar when cured in sulphate solution over that cured in pure water. At T3 (15%CP15%L), the mortar strength cured in water and sulphate solution were similar being 18.4 MPa and 17.9 MPa respectively. The T4 (30%CP20%L) mortars also gave similar strength as shown from the graph.

The reults indicate that T2 (10%CP20%L) gave a higher resistance to sulphate ingress than T1(20%CP10%L). This can be attributed to the dense nature of carboaluminate and calcium silicate hydrate formed within T2 mortar structure.

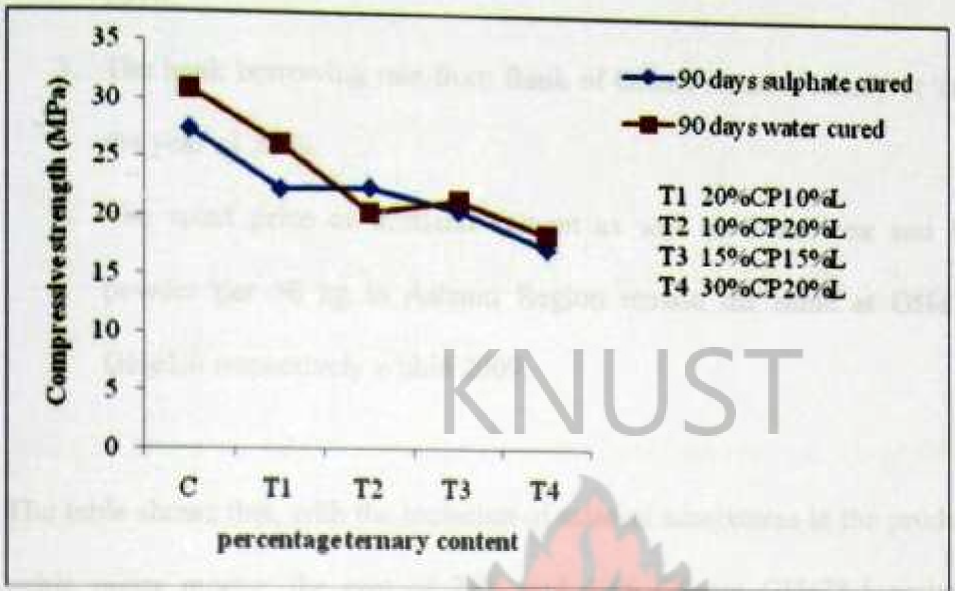

Figure 4.17: Compressive strength of ternary mortar mix cured in Na_2SO_4 and water for 90 days.

4.8 Economic analysis of plain and blended cement mortars.

As already illustrated in Figures 4.12 and 4.13, the optimum mix for a type M mortar was at either 25% clay pozzolana (CP) or 30% limestone (L) whereas that for a type S mortar was at 40% CP or 35% L, respectively. Table 4.4 gives the cost analysis per cubic meter (m^3) of plain and blended mortars. The cost analysis was based on the price of ordinary Portland cement and the mineral admixtures pertaining as of May, 2009.

- Cost of OPC per 50 kg = GH¢ 11.00
- Cost of CP or L per 50 kg = GH¢ 5.00

The economic analysis determined made use of the following assumptions:

1. The inflation rate remains steady at 16% from 2009 to 2010.
2. The Prime rate of Bank of Ghana remains constant at 14% between 2009 and 2010.
3. The bank borrowing rate from Bank of Ghana remains steady at 16% within the year of 2009.
4. The retail price of Portland cement as well as Pozzolana and Limestone powder per 50 kg in Ashanti Region remain the same at GH¢11.00 and GH¢5.0 respectively within 2009.

The table shows that, with the inclusion of mineral admixtures in the production of a cubic meter mortar, the cost of 25% and 40% CP are GH¢23.5 and GH¢37.61 respectively, whilst the cost of limestone content at 30% and 40% are GH¢28.23 and GH¢32.42, respectively.

The cost of ordinary Portland cement (OPC) in plain mortar per cubic meter as shown in table 4.4 is GH¢206.83. The inclusion of CP at 25% and 40% reduces OPC cost to GH¢155.12 and GH¢124.1 respectively, representing 25% and 40% of OPC cost reduction respectively. Similarly, the inclusion of limestone in a cubic meter mortar at 30% and 35% reduce OPC cost to GH¢144.72 and GH¢135.51 respectively. These also represent OPC cost reductions of 30% and 34%, respectively. The cost of sand as shown in the table which is used to produce a cubic meter mortar is almost similar with respect to the plain and blended mixes.

Table 4.4. Cost analysis of 1:3 mortar per m^3 of plain and blended mortar

Cost (GH¢)	1:3 mortar mix				
	Plain	CP		L	
	0%	25%	40%	30%	35%
Admixture	0	23.5	37.61	28.23	32.42
OPC	206.83	155.12	124.1	144.72	135.51
Sand	38.9	36.47	35.01	35.98	35.51
Total	245.73	215.1	196.72	208.93	203.48

CP = Clay pozzolana, L= limestone

It can be seen from table 4.4 that the overall cost of plain mortar per cubic meter was GH¢245.73. Clay pozzolana incorporation in a cubic meter mortar at 25% and 40% replacement of OPC give a total cost of GH¢215.1 and GH¢196.72, respectively, representing overall cost reductions of 12.5% and 20% respectively. Also limestone inclusion in a cubic meter mortar at 30% and 35% give an overall cost of GH¢208.93 and GH¢204.48 respectively which represent a reduction of 15% and 17% respectively.

The cost analysis from Table 4.4 proves that the use of 20% or 40% clay pozzolana (CP) or 30% or 35% limestone (L) to produce either a type M or S mortar has the potential to significantly reduce the cost of ordinary Portland cement and therefore influence the overall cost of producing mortars and concretes.

CHAPTER FIVE

5.1 CONCLUSIONS AND RECOMMENDATIONS

5.2 Conclusions

Based on the experimental results, data and the discussions already presented, the following conclusions are drawn:

1. Particle size analysis determined on OPC, CP and L revealed that the powder samples fall in the range of 0.0015-2.25mm, 0.0017-0.135mm and 0.0033-10.00mm respectively. These show that OPC is well graded whilst CP and L are uniformly graded.
2. The chemical characterization of CP verified that the summation of SiO_2, Al_2O_3 and SiO_2 is 81.23%, SO_3 is 0.14% and LOI is 10%. By ASTM standards, class N pozzolana is composed of a minimum of 70% for the sum of SiO_2, Al_2O_3 and Fe_2O_3, maximum of 4% for SO_3 and a maximum of 12% for LOI. This implies that CP is a class N pozzolana.
3. The chemical analysis of limestone verified that limestone powder from that portion of Orterkpolu reserve contains 88.5% $CaCO_3$. By EN 197-1 standards, the minimum $CaCO_3$ is 75%.
4. The mineral composition of CP reveals the presence of kaolinite, quartz and a small amount of goethite whereas limestone also confirms the presence of calcite, dolomite and a small amount of quartz.
5. The replacement of OPC by CP, L or both between 10% and 50% in a binary or ternary paste system generally demand more water than OPC paste.

6. Water demand of paste containing between 10% and 40% pozzolana shows a progressive increase with increase in pozzolana content. On the contrary, water demand of paste containing 10% to 30% of limestone content is steady, and increases with 35% to 40% limestone content.
7. It can be observed that in a binary paste mixture, CP and OPC mixtures demand more water than L and OPC mixtures at OPC replacement between 10 and 40% by CP or L.
8. In the ternary paste mixture, batch mixes that contain 20% pozzolana and 10% limestone demands more water than those that contains 10% pozzolana and 20% limestone. The batch mixes confirm that pozzolana addition to cement has a high water demand than limestone addition.
9. The initial setting time of paste that contains from 10% to 25% CP content is similar to OPC paste. It increases progressively beyond 25% and up to 40% CP content. For the final setting time, paste that contains 10% CP content seems to set faster, however between 20% and 40% CP content, the final setting time is increased as compared to the control paste.
10. Binary paste mixture containing limestone content between 10 and 40% replacement of OPC shows a retarded initial setting time as compared with OPC paste; however the final setting time is shorter than for OPC paste.
11. Ternary paste mixture which was prepared by replacing OPC with the combination of CP and L shows a longer initial setting time than OPC paste. The final setting times did not show any significant differences between the control paste and the ternary paste mixture.
12. In a binary mortar incorporating clay pozzolana, the 28-day compressive strength of mortar that contains 10% and 20% CP content is higher than

ASTM type M mortar of minimum strength of 20.0 MPa whilst between 30% and 40% CP content shows a 28-day compressive strength higher than ASTM type S mortar with minimum strength of 14.8 MPa. This means that 10 to 20% CP content can be used to produce type M mortar whereas 25 to 40% is best suitable for type S mortar.

13. The 28-day compressive strength of binary mortars that contain between 10% and 25% limestone content is higher than type M mortar strength and therefore best suitable for it, whereas from 30 to 35% content it is higher than type S mortar strength and can therefore be used appropriately to produce mortars of that class.
14. Optimum percentage replacement of OPC by CP or L to produce a type M mortar in a binary mortar system is either 20% or 25% respectively whilst to produce a type S mortar, the optimum OPC replacement by CP or L is 40% or 35% respectively
15. In a ternary mortar mixture, batch mixes that contain 20%CP10%L, 10%CP20%L and 15%CP15%L were more suitable to produce type M mortar whilst the batch mix which contains 30%CP20%L was suitable to produce a type S mortar.
16. The durability studies revealed that the 90-day compressive strength of binary mortars that contain 10% content of either CP or L content had the highest strength when the mortar cubes were cured in either water or 2% sodium sulphate solution. This shows that 10% content of either CP or L binary mortars has a higher resistance against the ingress of water or sulphate solution.

17. The durability test shows that for binary mortars containing CP content between 20% and 40%, sulphate attack has a mild effect on the compressive strength. This is also similar to binary mortars that contain limestone content between 20% and 40%.
18. In the durability analysis, ternary mortars that contain batch mixes of 10%CP20%L produce higher compressive strength than a batch mortar that contains 20%CP10%L. This shows that hydration compounds that are formed in the batch mix of 10%CP20%L probably led to a denser mass than batch mix of 20%CP10%L.
19. The use of limestone or pozzolana or both could produce cost effective masonry mortars over plain mortars. This is because replacing OPC by 25% pozzolana or 30% limestone to produce type M mortar could make savings of 12.5% and 15% respectively over plain mortars. Again replacing OPC by 40% pozzolana or 35% limestone produced type S mortars which could also make a saving of 19.9% and 17.2% respectively over plain mortar.

5.3 Recommendations

From the above conclusions, the following recommendations are made

- Further studies on 1:6 paste and mortar mixes should be investigated since that formulation is adopted by some builders and engineers for masonry works.
- Other limestone and clay deposits in Ghana should be explored and be used as mineral admixtures for cement replacement in mortar formulation.
- The aspect of durability studies which were carried out in this investigation should be determined beyond 90 days which was adopted in this work so as to ascertain sulphate effect on mortar over longer periods of curing, for example 180days, one year or beyond.

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