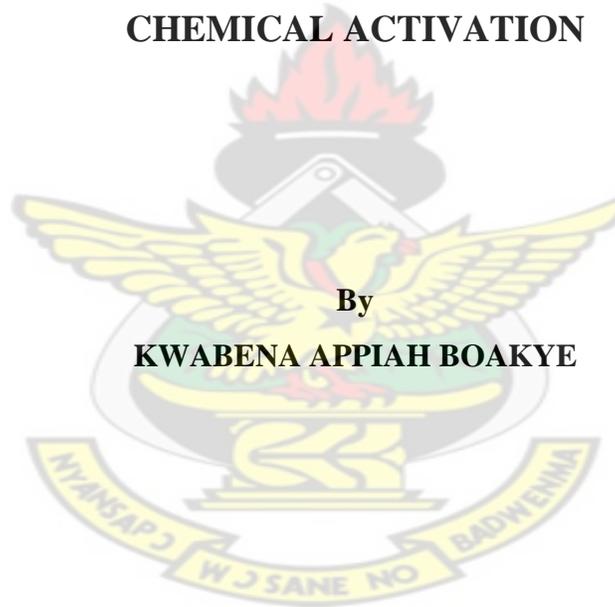


KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
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IMPROVEMENT OF SETTING TIME AND EARLY STRENGTH
DEVELOPMENT OF POZZOLANA CEMENT THROUGH
CHEMICAL ACTIVATION



By
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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE AWARD OF DEGREE OF MASTER OF SCIENCE IN
ENVIRONMENTAL RESOURCES MANAGEMENT

May 2012

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DECLARATION

It is hereby declared that this thesis is my own work towards the MSc. Degree and that, to the best of my knowledge, it contains neither material previously published by another person nor material which has been accepted for the award of any degree of the University, except where due acknowledgement has been made in the text.

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ABSTRACT

The use of clay pozzolana is being massively promoted in Ghana by CSIR-BRRI because of its technical, economic and to a large extent, environmental advantages. Work done with clay pozzolanas in Ghana indicate that by replacing approximately 30% by mass of ordinary Portland cement with burnt clay pozzolana through intimate mixing, the resulting Portland pozzolana cement (PPC) exhibits compressive strength values good for both load-bearing and non-load-bearing structural application. That notwithstanding, pozzolana cements are noted for their slow strength development resulting in low early strengths and slow nature of setting.

This study has investigated the improvement of setting times and early strength development of cement samples containing 10%, 20%, 30% and 40% clay pozzolana by chemically activating the samples with 1% - 4% CaCl_2 , Na_2SO_4 , and AlCl_3 . The physical, chemical and mechanical properties of the pozzolana cement at raw and hydrated state were studied. The results indicate that, 30% pozzolana cement activated with 2% Na_2SO_4 , 3% CaCl_2 or 4% AlCl_3 is able to improve early strengths by 28.4%, 28.4%, 26.8% respectively and 28-day strengths by 9.5%, 8.0% and 16.3%. Setting times were also accelerated to equal that of OPC by the addition of 2% Na_2SO_4 , 3% CaCl_2 or 4% AlCl_3 . The study therefore showed that the addition of Na_2SO_4 , CaCl_2 or AlCl_3 could greatly improve the early strength development and significantly reduce the setting time of pozzolana cement. Water permeability of pozzolana cement decreased as chemical activator concentration increased from 1% - 4%.

The economic analysis reveals that chemical activation of pozzolana cements is economically viable as the activation with Na_2SO_4 , CaCl_2 or AlCl_3 gives similar strengths as OPC. The activation of 30% pozzolana cement with 2% Na_2SO_4 , 3% CaCl_2 or 4% AlCl_3 slightly increases the unit cost of pozzolana cement but still about 16.7%, 16.2% or 13.1% less expensive than OPC.

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DEDICATION

This work is dedicated to my beautiful wife, Gloria Boakye, and my lovely daughter, Kayla Adepa Amankwah Boakye. Your love and support is greatly appreciated.

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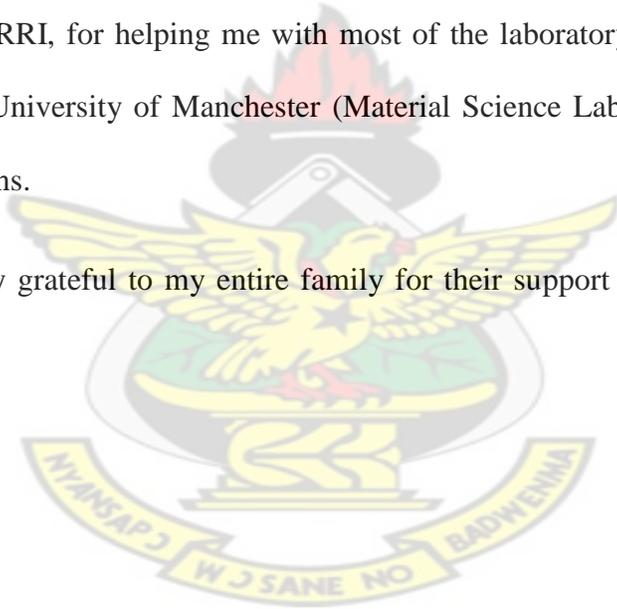


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CHAPTER ONE

INTRODUCTION

Cement is the most widely used construction material throughout the world. This leads to an enormous production of cement to meet the increasing demand for housing and infrastructure. Cement production is however harmful on the environment due to carbon dioxide emission. Reducing cement production while maintaining sustainable development has been an important issue in the development of construction materials. Replacing Portland cement with percentages of pozzolana has been reported as a good alternative.

Each year, the concrete industry produces about 12 billion tonnes of concrete and uses about 2.86 billion tonnes of Portland cement worldwide (Global Cement Report, 2010).

Indeed, with the manufacture of one tonne of cement, approximately 0.8 tonne of CO₂ are released into the atmosphere. About 50% of the CO₂ produced during cement manufacture is due to fossil fuel consumption and the rest due to the calcination of the limestone (Claus and Guimaraes, 2007). The cement industry accounts for 5 – 8% of global CO₂ emission. This makes the cement industry the second largest producer of this greenhouse gas (Scrivener and Kirk, 2007). Also the SO₃ and NO_x released as a result of Portland cement manufacture can cause serious environmental impact such as greenhouse effect and acid rain (Dongxu et al, 2000).

It is obvious that minimization of production of Portland cement clinker would greatly help to reduce the CO₂ emission produced by the cement industry. One wise solution is to promote the usage of pozzolanic materials in mortar and concrete works thereby reducing

the world's demand for Portland cement which eventually reduces the emission of CO₂ into the atmosphere.

Work done with clay pozzolanas in Ghana indicates that by replacing approximately 30% by mass of ordinary Portland cement with burnt clay pozzolana with intimate mixing, results in Portland pozzolana cement (PPC) which exhibits compressive strength values good for both load-bearing and non load-bearing structural applications (Atiemo, 1992, 1998).

Pozzolanic materials when used in mortar and concrete works improve durability which is the ability of concrete to resist weathering action, chemical attack and abrasion. Pozzolanic materials also bring in other technical advantages such as low heat of hydration and high ultimate strength. The higher strength of concrete with pozzolanas at later ages is as a result of the pozzolanic reactions increasing the amount of calcium silicate hydrates (C-S-H) while diminishing Ca(OH)₂ (Helmuth, 1987).

That notwithstanding, pozzolana cements are noted for their slow strength development resulting in low early strengths as shown in Figure 1.1. For replacement level up to 30%, the strength at ages about 3 to 6 months will often exceed that of Portland cement concrete.

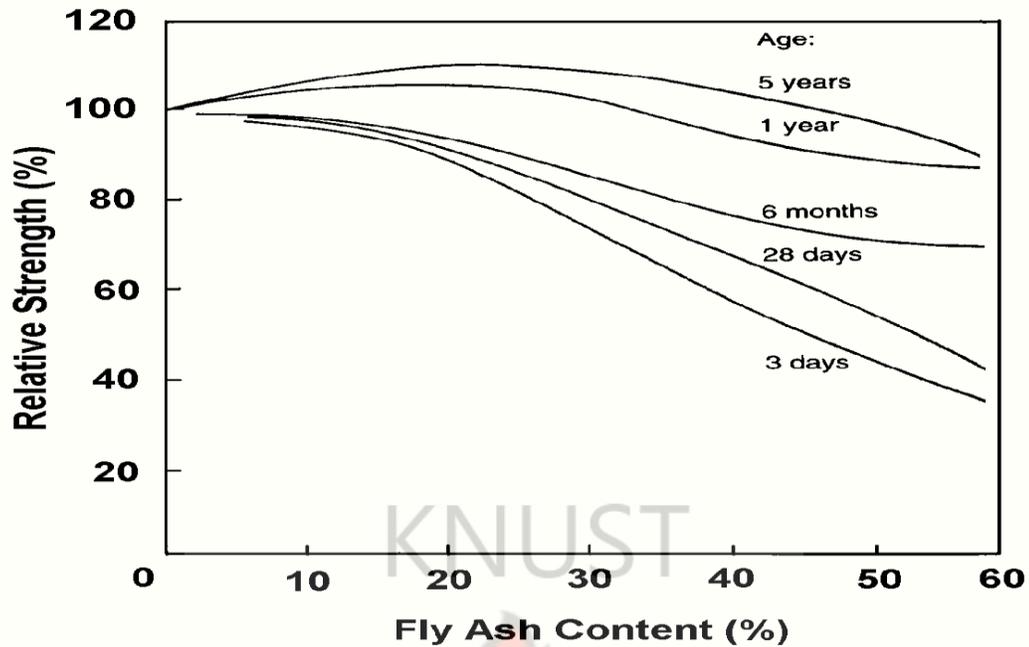


Figure 1.1: Effect of fly ash content and age on strength development of concrete
(Source: Neville, A. M., 1981)

They also exhibit slow rate of setting and hardening. These undesirable properties rise from the slow reaction rate of the active pozzolana constituents with the liberated $\text{Ca}(\text{OH})_2$ from the Portland cement (Lea, 1970a). It is estimated that the extent of reaction of pozzolana is only about 20% at 90 days, compared with 80% for Portland cement (Shi, 2001). Due to the pozzolanic reactions between lime and constituents of pozzolana, the free lime content in pozzolana cement or concrete decreases with time (Fig. 1.2) depending on the content and nature of the pozzolana in the cement and concrete.

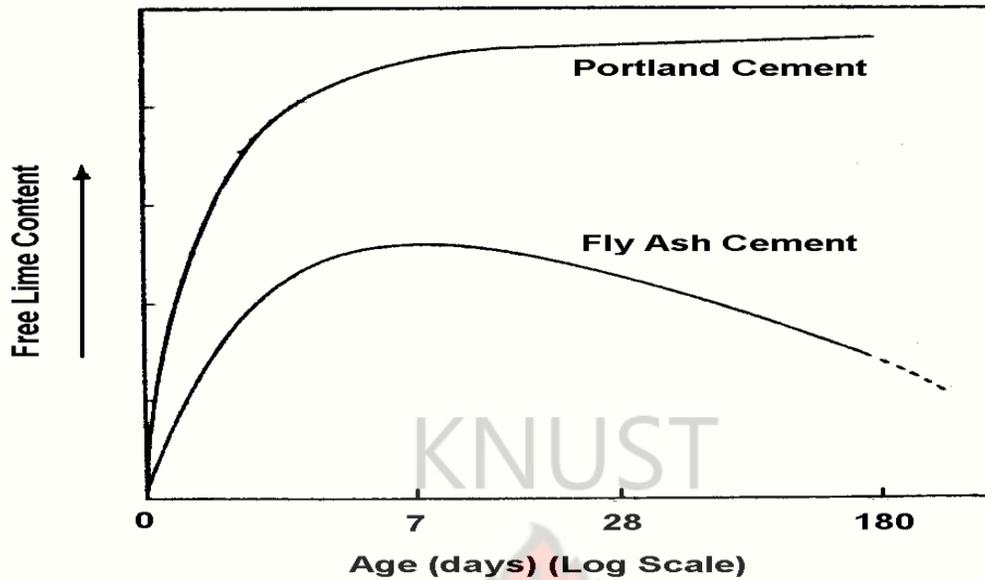


Figure 1.2: Schematic illustration of free Ca(OH)_2 content in Portland and pozzolana cement. (Source: Shi and Shao, 2002)

Early strength is a critical measure in concrete industry since it determines the speed of construction. Therefore, low early strength development is an obstacle in promoting pozzolana usage as Portland cement replacement. In order to overcome slow early strength development and high setting times in pozzolanic materials, techniques such as thermal activation, mechanical activation and chemical activation have been proposed in literature.

Mechanical activation (prolonged grinding) can increase the reactivity of pozzolana to some extent. Grinding, however, is an energy intensive process and needs complicated facilities. Spherical pozzolana particles are broken during grinding, which will result in higher water demand for a given workability and thus somewhat offset the improvements in reactivity due to grinding (Shi and Shao, 2002). Also, elevated temperature curing

increases the strength development rate, but decreases the ultimate strength of concrete (Shi and Shao, 2002) and could be very expensive.

A comparison based on strength-cost relationship indicates that the addition of chemical activators into concrete and mortar mixtures is the most simple, efficient and inexpensive technique for enhancing reactivity of pozzolana cement (Shi and Day, 2001).

This study seeks to investigate how the setting time and early strength of pozzolana cements can be improved by the application of chemical activators such as CaCl_2 , Na_2SO_4 , and AlCl_3 . In chemical activation, the pozzolana cement is treated with a chemical compound solution before the mortar or concrete is prepared. The chemical compound, as a separate ingredient, can also be dissolved in the water to be used to prepare the mortar or concrete.

1.1 Main objective

The main objective of this study is to improve the early strength and setting times of clay pozzolana cement for construction by the application of chemical activators.

1.1.1 Specific objectives

To achieve the main objective, the following specific objectives were set:

- i. Chemically activate the pozzolana cement using different chemical compounds at different concentrations.
- ii. Determine the following:

- physical, chemical and engineering properties of the Ordinary Portland Cement (OPC), clay pozzolana and pozzolana cements.
 - X-ray diffraction (XRD) of OPC and pozzolana.
- iii. Compare the effect of the various chemical activators on setting and strength of cement.
- iv. The economic viability of chemically-activated pozzolana cement.

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CHAPTER TWO

LITERATURE REVIEW

2.1 Pozzolana

Pozzolana is defined as a siliceous or alumino-siliceous material that, in finely divided form and in the presence of moisture, chemically reacts at ordinary room temperature with calcium hydroxide, released by the hydration of Portland cement, to form compounds possessing cementitious properties (Canadian Standard Association, 2000). Pozzolanic materials can be used either as an addition to the cement in the manufacturing process or as a replacement for a portion of the cement in the mortar and concrete production.

The early known use of pozzolana dates back to the ancient times. Lime-natural pozzolana mixtures were used in the masonry construction of aqueducts, bridges, retaining walls and buildings during Roman times. These binders were strong and durable and had been used for centuries by different cultures all over the world. The invention of Portland cement in the 19th century resulted in the reduction in the use of lime-pozzolana binders. Today, pozzolanas are used in combination with Portland cement due to their additional technical benefits.

Pozzolanas can be classified as natural and artificial. The basic classification into natural and artificial has no real or engineering purpose. With respect of economy and performance, it does not matter whether the source is “natural” or not (Day, 1990). Natural pozzolanas are of two types: the true natural pozzolanas and the pseudo natural pozzolanas.

The true natural pozzolanas are ashes and lavas originating from alkalitrachytic, leucitic, leucotephritic and hauynophric types of magma. These ashes result from explosive eruptive volcanoes and are forced to solidify as a pyroclastic glass (glass fragments formed by rapid quenching of magma produced by volcanic explosions) (Malquori, 1960). In the pseudo natural pozzolanas, the pyroclastic glassy minerals in the original lava have undergone hydrothermal alteration (auto-metamorphism) leading to zeolitization and sometimes argillization (Malquori, 1960, Steopoe, 1964, Kemser, 1964).

Artificial pozzolanas are those materials in which the pozzolanic property is not well developed and hence usually have to undergo pyro-processing before they become pozzolanic (Hammond, 1983). Artificial pozzolanas include materials such as flyash, blast furnace slag, surkhi (burnt clay), siliceous and opaline shales, spent oil shale (used in Sweden to make “gas concrete”), rice husk ash, burnt sugar cane stalks and bauxite waste (Grane, 1980).

The general term pozzolana is used to designate natural as well as industrial co-products that contain a percentage of vitreous silica. This vitreous (amorphous) silica reacts at ambient temperature with the lime produced by the clinker minerals to form hydrated calcium silicates (C-S-H) (Venuat, 1984, Malhotra, 1987, Malhotra and Mehta, 1996).

Table 2.1 presents the chemical composition of some natural pozzolanas.

Table 2.1: Chemical composition of some natural pozzolanas

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	SO ₃	CaO	Fe ₂ O ₃	LOI	Total
Sacrofano (Italy)	-	-	3.05	89.22	-	2.28	0.77	4.67	-	99.99
Bacoli (Italy)	3.08	1.2	18.20	53.08	0.65	7.61	9.05	4.29	3.05	100.24
Segni (Italy)	0.85	4.42	19.59	45.47	6.35	0.16	9.37	9.91	4.03	100.05
Santorin Earth	3.80	2.00	13.00	63.80	2.50	-	4.00	5.71	4.80	99.60
Rhenish trass	1.48	1.20	18.29	52.12	-	5.06	4.94	5.81	11.10	100.00
Rhyolite pumice	4.97	1.23	15.89	65.75	1.92	-	3.35	2.54	3.43	99.07

(Source: Taylor, 1997)

2.1.1 Calcined clay pozzolanas

When clay is calcined at a temperature of 700 to 750 °C, the clay is dehydrated and its crystalline structure is totally disorganized. In doing so the water molecules are driven off and a quasi-amorphous material is obtained. Active silica tetrahedral then reacts with the lime liberated by the hydration of C₃S and C₂S of Portland cement (Massazza, 1998). However the addition of calcined clay increases the water demand in concrete.

Most calcined clay pozzolanas contain silica (SiO₂) in excess of 50% as the most active constituent. Other important constituents are the alumina (Al₂O₃) and hematite (Fe₂O₃) (commonly referred to as total R₂O₃) which usually exceed 20%. An important criterion for a good burnt clay pozzolanas as well as most other pozzolanas in terms of constituents is that the sum of SiO₂, Al₂O₃ and Fe₂O₃ contents should exceed 70% (Lea, 1940; ASTM C 618, 2000).

Research on various Ghanaian clay deposits has shown that such clay pozzolanas when milled to cement fineness can replace up to 30% of ordinary Portland cement in structural applications. These clay pozzolana-cement mixes have been successfully used for various housing construction projects in Ghana (Atiemo, 2005). Table 2.2 shows the properties of some Ghanaian clay pozzolana-cement mortars.

Table 2.2: Engineering properties of Ghanaian clay pozzolana-cement mortar

Sample	Pozzolana content, %	Setting time, min		Water absorption, %	28 days compressive strength, Mpa
		Initial	Final		
Asokwa	30	83	208	1.8	31.4
Hwereso	25	92	262	2.5	24.1
Mankranso	30	85	225	1.9	29.9
Mfensi	30	212	310	2	30.5
Mankessim	30	90	250	2.2	29.1
Nkonsia	30	75	194	1.8	28.4

(Source: Atiemo; 2005)

2.2 Portland cement

Cement is defined as a powdered material that chemically reacts with water and therefore attains the property of setting and hardening (Neville, 1996). This property makes the cement hydraulic. Portland cement is made by heating raw materials with an appropriate chemistry, usually mixture of limestone and clay, to a temperature between 1400°C and 1600°C, where the two materials interact chemically to form the calcium silicates. Partial fusion occurs, and nodules of clinker are produced. The clinker is mixed with a few percent of calcium sulphate and finely ground, to make the cement.

Limestone + Clay \longrightarrow Clinker + 2% gypsum \longrightarrow Portland cement

Some modern cement specifications, EN 197-1, also permit adding up to 5% limestone in the course of clinker grinding. The calcium sulphate, which is commonly described as gypsum, controls the rate of set and influences the rate of strength development. The clinker chemically has a composition of CaO, SiO₂, Al₂O₃, and Fe₂O₃, all constituting about 80% of Portland cement. The other significant minor oxides are MgO, SO₃, K₂O and Na₂O (Lea, 1970). Cement clinker particles are multiphase solids. Each phase has a specific reaction with water to produce a range of hydration products.

Alite (C₃S) is the most important constituent of all normal Portland cement clinkers and it constitutes 50-70% of the total composition of the clinker. It is tricalcium silicate (Ca₃SiO₅) modified in composition and crystal structure by ionic substitutions. It reacts relatively quickly with water, and is the most important of the constituent phases for strength development up to 28 days. Belite (C₂S) constitutes 15-30% of normal Portland cement clinkers. It is dicalcium silicate (Ca₂SiO₄) and normally presents wholly or largely as β polymorph. It reacts slowly with water, thus contributing later-age strength beyond 28 days (Taylor, 1997).

Aluminate constitutes 5-10% of most normal Portland cement clinkers. It is tricalcium aluminate (3CaO.Al₂O₃), substantially modified in composition and sometimes also in structure by ionic substitutions. It reacts rapidly with water, and can cause undesirably rapid setting unless a set-controlling agent, such as gypsum, is added (Taylor, 1997).

Ferrite makes up 5-15% of normal Portland cement clinkers. It is tetracalcium aluminoferrite ($\text{Ca}_2\text{AlFeO}_5$), substantially modified in composition by variation in Al/Fe ratio and ionic substitutions. The rate at which it reacts with water appears to be somewhat variable, perhaps due to differences in composition or other characteristics, but in general is high initially and low or very low at 28 days (Taylor, 1997). Table 2.3 shows the compositions of phases in Portland cement clinker.

Table 2.3: Typical compositions of phases in Portland cement clinkers (mass percent)

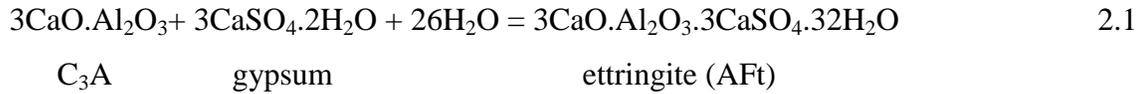
Phase	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	Mn ₂ O ₃	Fe ₂ O ₃
Alite	0.1	1.1	1	25.2	0.1	0.1	0.1	71.6	0	0	0.7
Belite	0.1	0.5	2.1	31.5	0.1	0.2	0.9	63.5	0.2	0	0.9
Aluminate (Cubic)	1	1.4	31.3	3.7	0	0	0.7	56.6	0.2	0	5.1
Ferrite	0.1	3	21.9	3.6	0	0	0.2	47.5	1.6	0.7	21.4
Aluminate (Orthorhombic)	0.6	1.2	28.9	4.3	0	0	4	53.9	0.5	0	6.6
Aluminate (Low Fe)	0.4	1	33.8	4.6	0	0	0.5	58.1	0.6	0	1
Ferrite (Low Al)	0.4	3.7	16.2	5	0	0.3	0.2	47.8	0.6	1	25.4

(Source: Taylor, 1997)

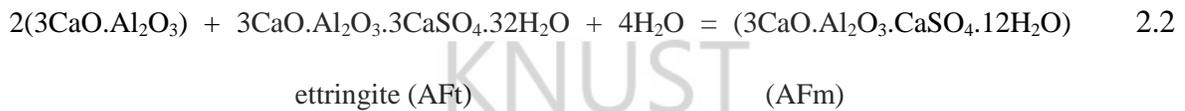
2.2.1 Hydration of Portland cement

The chemical reaction between cement minerals and water is mainly by hydration. The active cement components are tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$ or C_3A); tetracalcium-aluminoferrite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ or C_4AF); tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$ or C_3S) and dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$ or C_2S). The factors responsible for the mechanical properties of concrete are the extent of hydration of cement and the resultant microstructure of the hydrated cement. In contact with water, the C_3A and C_4AF react almost instantaneously leading to the setting of the cement. Both the C_3A and the C_4AF

react with calcium sulphate to produce ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$). The overall non-stoichiometric reaction and their product can be represented as:



This hydrates further to form a solid solution of the low-sulphate sulphoaluminate— $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$ usually existing in a solid solution with C_4AH_{13} (Lea, 1998).



Concurrently, C_3S and C_2S react with water, albeit more slowly producing afwillite ($3\text{CaO}\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O}$) and lime, $\text{Ca}(\text{OH})_2$. This process continues up to more than one year and leads to hardening of the cement paste though there are bound to be unhydrated cement cores (Ashby and Jones, 1986). The overall non-stoichiometric reactions that lead to hardening of the cement products can be represented as:

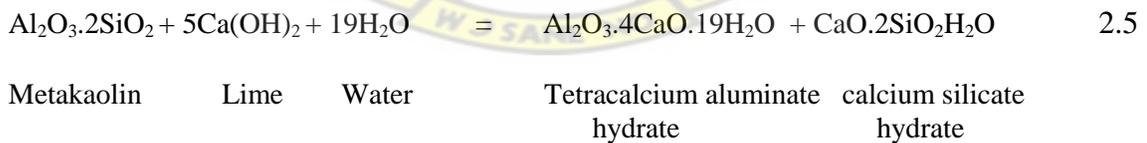


The afwillite and the lime produced by these reactions remain in solution and in the presence of water, further hydrolyze to produce more lime in solution (Lea, 1970a). The lime thus produced is a source of weakness in cement products, especially concrete for several reasons. The free lime has a low strength and poor stability — leading to lower strength and less durability of cement paste and concrete (Pu, 1999). The free lime, on

account of its low stability, is also easily attacked by sulphate solutions. Additionally, by a preferential growth in one direction in the presence of water, the free lime crystals may cause unsoundness in cement products especially in mass concrete leading to disruptions and failure of structures, several years after setting (Lea, 1970a).

2.3 The pozzolanic reaction

When pozzolana is mixed with Portland cement to produce pozzolana cement, the silica in the pozzolana combines with the free lime released during the hydration of cement. This action is called pozzolanic action. The pozzolanic activity is due to the presence of fairly divided glassy silica and lime which produces calcium silicate hydrate (C-S-H), C_2ASH_8 (gehlenite hydrate) and C_4AH_{13} (tetracalcium aluminate hydrate) as given in the equation below. The formation of secondary C-S-H by this reaction reduces total porosity and refines the pore structure, improving the strength and impermeability of the cementitious matrix (Siddique and Khan, 2011 , Singh and Garg, 2006).



The optimum replacement percentage of cement with clay pozzolana is associated with the changes in the nature and proportion of the different reaction products, temperature, and reaction time. Hydration reaction depends upon the level of reactivity of pozzolana in terms of the processing conditions and purity of feed clay. The feed clay (kaolin) should be

either naturally pure or refined by standard minerals processing techniques; otherwise the impurities would act as diluents (Kostuch *et al*; 1993). Reactivity level of clay pozzolana (metakaolin) can be determined by Chapelle test (Asbridge *et al*; 1994). It is expressed as consumption rate of calcium hydrate per gram of pozzolanas. The amount of Ca(OH)_2 in hardened concrete can be determined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

Kostuch *et al* (1993), observed that Ca(OH)_2 as significantly reduced with age for all replacement levels (0, 10, 20%); and 20% by metakaolin was required to fully remove all the Ca(OH)_2 in concrete at 28 days whereas Oriol and Pera, 1995, reported that between 30% and 40% metakaolin is required to remove all the Ca(OH)_2 in metakaolin-Portland cement paste at a water-binder ratio of 0.5 when cured in lime-saturated water for 28 days. Table 2.4 shows the pozzolanic activity of silica fume (SF), fly ash (FA) and metakaolin (MK).

Table 2.4: Pozzolanic activity of various pozzolana

Pozzolana	Silica fume	Fly ash	Metakaolin
$\text{Ca(OH)}_2/\text{Pozzolana}$ Reactivity (mg)	427	875	1,050

(Source: Asbridge *et al*; 1994)

Ambroise *et al* (1994), studied the early hydration period of pastes containing metakaolin using isothermal calorimetry and conductivity. Differential thermal analysis, X-ray diffraction, and Fourier transform infrared spectrometry were used to estimate the

consumption of calcium hydroxide and identification of reaction products. The results showed that $\text{Ca}(\text{OH})_2$ was quickly consumed, the microstructure was rich in calcium silicate hydrates (CSH) and stratlingite (C_2ASH_8), and the pore size distributed displaced toward smaller values. At up to 30% replacement, metakaolin acted as an accelerating agent, the pore size distributed was displaced toward small values, and the $\text{Ca}(\text{OH})_2$ content was considerably reduced. Poon *et al* (2001) reported the degree of pozzolanic reaction in pozzolana-cement paste made with 5, 10, and 20% metakaolin. The results (Table 2.5) of the pozzolanic reaction of the pastes, represented as percentage value of the reacted pozzolana relative to the initial amount of the pozzolana in the paste. Based on the test results, it was concluded that; the degree of reaction of pozzolana at each age was high at replacement level of 5% than at the replacement levels of 10 and 20%. The higher rate of pozzolanic reaction in cement pastes with a lower replacement level can be attributed to the higher concentration of $\text{Ca}(\text{OH})_2$ available for the pozzolana to react with. Secondly, although the rate of pozzolana reaction became slower after prolonged curing, there was still a considerable increase in the degree of reaction of pozzolana from 28 days to 90 days. For cement paste with 10% pozzolana, the degree of reaction of pozzolana was 36.3% at 28 days. The reaction of pozzolana was not completed at the age of 90 days and about half of the pozzolana remained unreacted. Table 2.5 shows the degree of reaction of blended cement pastes.

Table 2.5: Degree of reaction of blended cement pastes

Pozzolana replacement (%)	Degree of reaction of pozzolana, %			
	3 days	7 days	28 days	90 days
5	20.56	29.52	39.44	56.28
10	15.34	26.98	36.28	50.96
20	9.38	18.64	30.82	41.99

(Source: Poon, 2001)

2.4 Activation of Pozzolanas

The substitution of Portland cement with pozzolanas reduces the strength obtained at the earlier ages (2 and 7 days), up to 28 days. This effect is attributed to the low surface activity of the pozzolana at early ages. The low activity of pozzolanas can be attributed to the fact that the glassy surface layer of pozzolanas is dense and chemically stable. This layer prevents the interior constituents which are porous and amorphous and therefore more reactive from taking part in the pozzolanic reaction and also the silica-alumina chain of pozzolanas is firm and must be broken if activity is to be enhanced (Yueming Fan *et al.*, 1999).

The addition of pozzolanas has some major drawbacks particularly when speed is needed in the construction projects. It leads to prolonged setting times and lower early strength when compared to pure Portland cement. For a given binder content, early strength decreases with a retarded setting time as the quantity of pozzolana increases. To overcome this problem and increase pozzolanic activity rate various methods have been proposed through extensive research (Shi, 2001).

The early strength of pozzolana-cement mortar and concrete can be substantially raised by three processes of treatment; namely, thermal, mechanical and chemical activation.

2.4.1 Thermal activation

Pozzolanic materials, which are unreactive in their natural state, can be made chemically active by heat treatment. This can be achieved by either calcination of the raw material or elevated temperature curing of the product containing natural pozzolana. Some clay minerals possess pozzolanic property when treated with heat. A good example to the calcinations is metakaolin which is a very reactive pozzolana and marketed commercially. The raw material of the metakaolin is kaolin which exhibits no pozzolanic property in its natural form. By heat treatment the crystal structure of the clay minerals is disrupted and an amorphous or disordered alumino silicate structure is formed leading to pozzolanicity (Aldemir, 2006). The effect of calcination on the pozzolanic reactivity of natural pozzolana is highly dependent on the material and varies with different pozzolanas. The second thermal activation method is the curing of concrete with elevated temperatures. Based on Arrhenius formula (Shi and Shao, 2002) which describes the effect of temperature on reaction kinetics, it was found that the hydration of lime-pozzolana mixtures is more susceptible to temperature than that of Portland cement. The research has indicated that the samples containing natural pozzolana show significantly early strength increase when cured at elevated temperatures (Shi, 2001). Nevertheless, elevated temperature curing needs additional equipment and is usually suitable for precast products. It also consumes significant amount of energy (Shi and Day, 2001).

Several studies have indicated that an increase in curing temperature can significantly accelerate the hydration and strength development of cement and concrete containing fly ashes. Shi and Day (1993) studied this effect on strength development of cement mortars with and without pozzolana. At 20°C, the fly ash cement mortars displayed much lower strength than the Portland cement mortars from 3 to 28 days. When the curing temperature was increased from 20°C to 40°C, the fly ash cement mortars even had slightly higher strength than the Portland cement mortars at 14 days. However, at a very high curing temperature, fly ash cement may result in lower strength because monosulphaluminate (AFm) forms instead of ettringite (AFt) (Shi and Day, 1993). Figure 2.1 shows the effect of curing temperature on strength development of mortar with or without fly ashes.

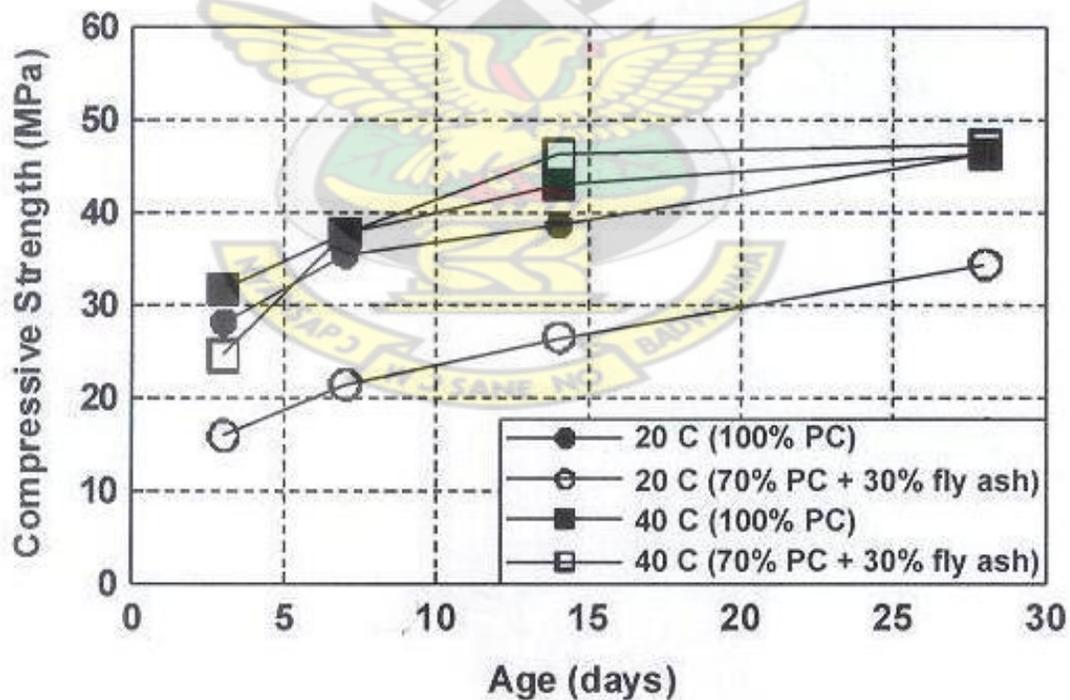


Figure 2.1: Effect of curing temperature on strength development of mortars with and without fly ashes (Paya *et al*, 2000)

Oriol and Pera (1995) investigated the effect of a microwave curing on lime consumption in pozzolana blended cements. The results were compared with those obtained at room temperature. It was concluded that pozzolanic reaction of pozzolana could be consequently promoted by microwave heating. As heat is generated quickly inside the cementitious material, thermal acceleration of the reaction was more efficient, allowing both reduction of pozzolana (15% instead of 30-40%) in normal conditions and of the water:cement ratio (0.40 instead of 0.50).

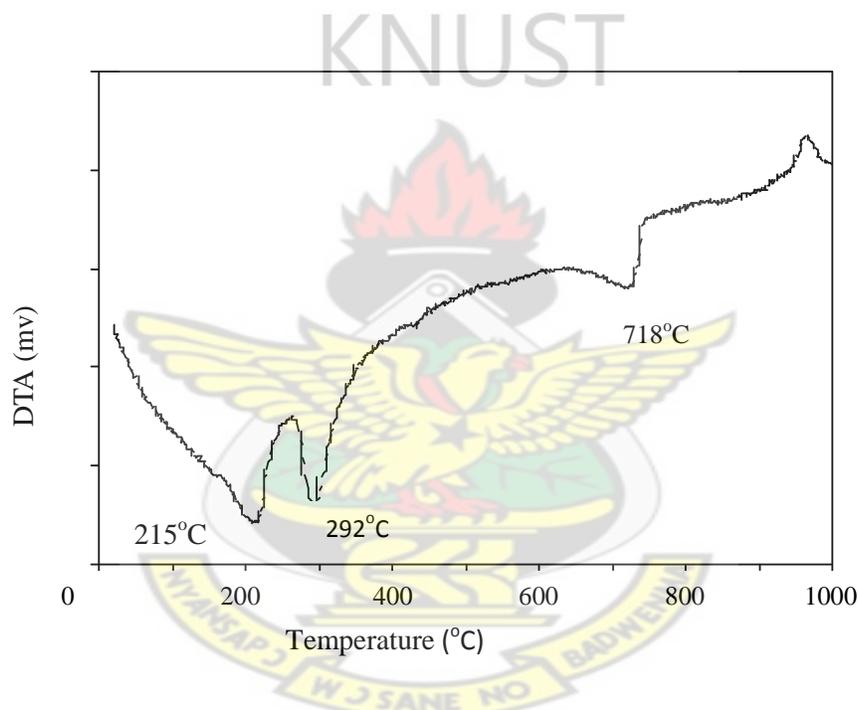


Figure 2.2: DTA curve for MK /lime paste (Rojas, 2006)

Rojas (2006) determined the effect of curing temperature on the reaction kinetics in metakaolin/lime mixture cured at 60°C and after 6 months of hydration. The stability of hydrated phases formed during the pozzolanic reaction was evaluated. The results exhibited that metastable hexagonal phases (C_2ASH_8 and probably C_4AH_{13}) coexist with stable cubic phase (hydrogarnet) in the absence of lime.

Also, there was evidence of the possible presence of a calcium aluminum silicate hydroxide hydrate (vermugite). DTA curve (Figure 2.2) showed the presence of CSH and the coexistence of metastable and stable phases in a metakaolin/lime system cured at 60°C for 6 months of hydration. The metastable phase was assigned to stratlingite (C_2ASH_8) and probably to C_4AH_{13} . The stable phase was attributed to katoite, a hydrogarnet structured phase. XRD pattern confirmed the presence of stratlingite and katoite as main crystalline compounds present under tested condition.

2.4.2 Mechanical activation

Mechanical activation of cements refers to prolonged grinding of the cement to increase its surface area. The rate of chemical reaction between two materials increases as the surface area available for the reaction increases. Likewise maximum pozzolanic reactivity is attained with the extended grinding times since the surface area increases as the material gets finer. It is again the nature of the pozzolanic material controlling the overall behavior. However, it is generally accepted that the early strength is enhanced with the use of finer natural pozzolana. However, mechanical activation of natural pozzolana also consumes extra energy and reduces grinding productivity. It is stated that, the increase of each $10m^2/kg$ Blaine fineness increases grinding cost by 10% (Nanjing, 1985). Figure 2.3 gives the relationship between pozzolanic activity index with cement and specific surface area of fly ash.

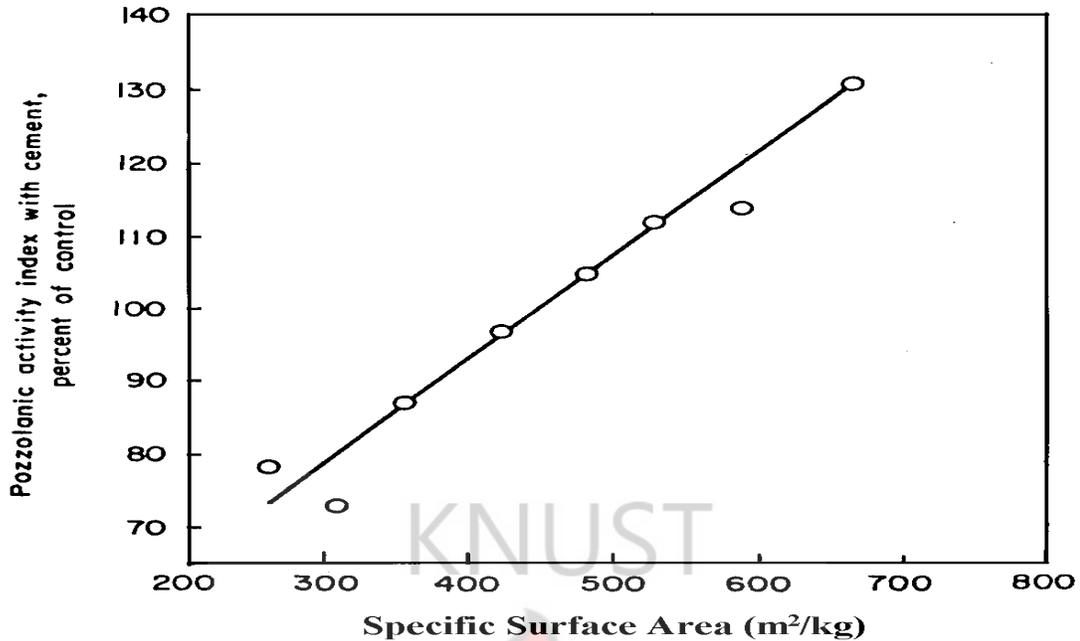


Figure 2.3: Relationship between pozzolanic activity index with cement and specific surface area of fly ash. (Source: Ravina, 1980)

Many researchers have dealt with the effect of grinding on reactivity of various cementitious and pozzolanic materials. Prolonged grinding increases not only the surface area of a material, but also the number of imperfection or active centers which exist at the edges, corners, projections and places where the interatomic distances are abnormal or are embedded with foreign atoms. These centers are in a higher energy state than in the normal structure. The more the active centers, the more reactive the pozzolana is (Dave, 1981). Millers and Oulton (1970) observed that percussive dry-grinding can cause obvious crystal distortion of kaolinite. It has been found that impaction and friction milling of high alumina cement alter its crystallinity and notably modifies its hydraulic behavior (Scian *et al*, 1991).

In an early investigation on the reactivity of six siliceous rocks, Alexander (1960) observed that siliceous materials such as quartz and basic or devitrified volcanic rocks, which are not regarded as likely sources of active pozzolana, become highly reactive when ground into ultrafine powders. This is due to the presence of a disturbed layer of highly reactive material, which is formed on the surface of the mineral particles as a result of prolonged grinding. However, if grinding is sufficiently prolonged, an upper limit of activity is attained, beyond which continued increase in surface area does not produce any further increase in pozzolanic reactivity.

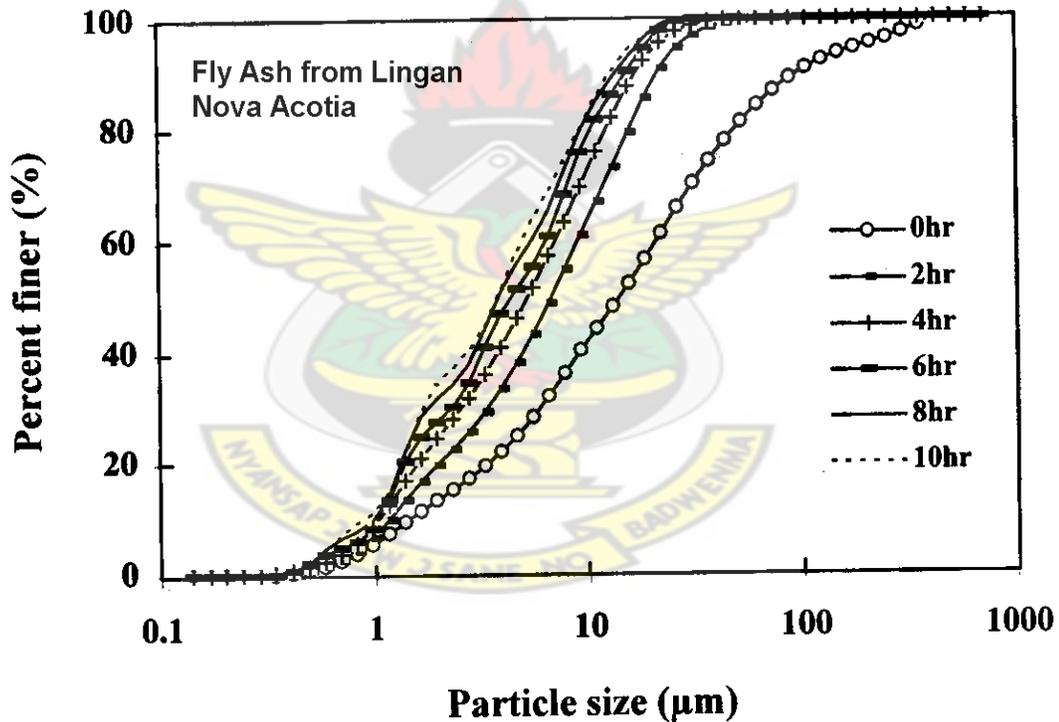
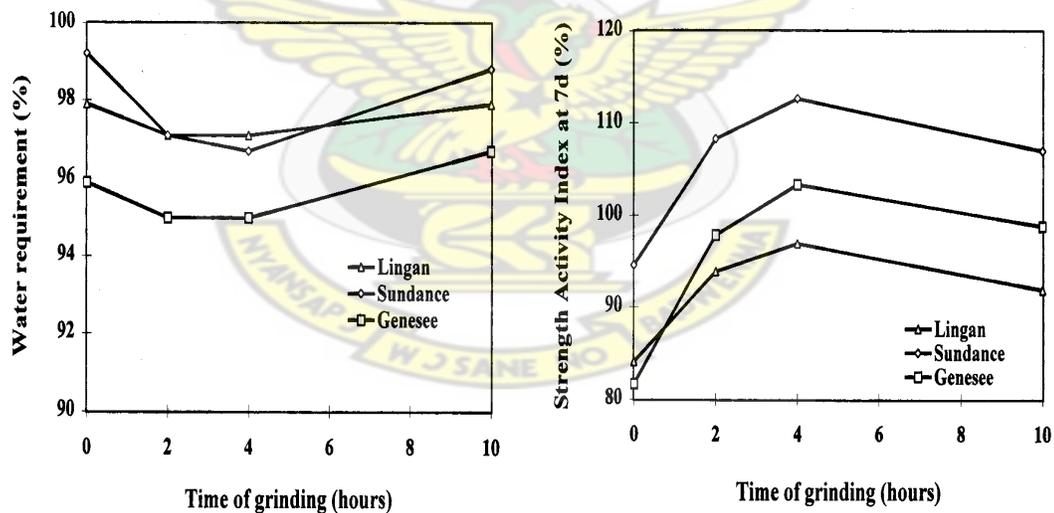


Figure 2.4: Effect of Grinding on Particle Size Distribution of Fly ash
(Source: Bouzoubaa, 1997)

A recent study indicated that the strengths of lime-natural pozzolana cements are linearly proportional to the Blaine fineness of the natural pozzolan (Day and Shi, 1994). Figure 2.4 describes the effect of grinding on particle size distribution of fly ash. A short period of grinding may further decrease the water requirement of fly ash cement due to the break up of plerospheres (Fig. 2.5-a). Prolonged grinding will increase the water requirement due to the increase of irregular-shape particles. When a fly ash is too coarse to meet the fineness requirement, grinding can be a solution. The results in Fig.2.5-b indicates a proper grinding increases the strength activity index, as determined following ASTM C311, by 15-27% at 7 days. Prolonged grinding decreases the strength activity index probably due to the increase of water requirement.



(a) Water Requirement

(b) Strength Activity Index

Figure 2.5: Effect of Grinding on Water Requirement and Strength Activity Index of Fly Ashes. (Source: Bouzoubaa, 1997)

Sarfo-Ansah (2010) investigated mechanical activation of Mfensi clay pozzolana with a replacement ratio of 30, 35, 40, and 50% using hammer milling, 24h ball milling, 36h ball milling, and roll milling. Generally, compressive strengths increased with curing period, as was expected. Although at the pozzolana mortar cubes were weaker than OPC mortar cubes at all replacements, their compressive strengths increased more rapidly after 28 days curing, than that of OPC. Milling of the Mfensi pozzolana substantially increased the compressive strength at all replacement ratios. The finer the pozzolana particles were, the higher the compressive strengths became. Thus, the highest compressive strength values were obtained for the roll milled pozzolanas, followed by the 36 h ball milled pozzolana. The lowest compressive strengths were obtained using hammer milling. Table 2.6 represents the compressive strengths of Mfensi pozzolana cement mortar cubes.

Comparing compressive strengths at 28 days, with hammer milling as a basis, roll milling resulted in 65-66% strength increase at 30 and 35% cement replacement, 52% increase at 40% cement replacement and 23% increase at 50% cement replacement. The 90-day compressive strengths were generally 45-55% higher for both 36 h ball milling and roll milling above that of hammer milling.

As expected, the early age compressive strengths (Table 2.6) decreased as the pozzolana content increased in the pozzolana cement mortars. However, except for hammer milling and 24hr ball milling, all the Mfensi pozzolana cement samples up to 50% replacement satisfied the early strength requirement of the European standard EN 197-1 for 2 and 7 days of 10.0 and 16.0 MPa respectively.

Table 2.6: Compressive strengths of Mfensi pozzolana cement mortar cubes

Milling type and period	Compressive strength, MPa			
	2 days	7 days	28 days	90 days
<u>Control</u>				
	19	36.3	43.9	47.1
<u>30% cement replacement</u>				
Hammer milling	14.7	18.2	24.5	29.4
24 h Ball milling	16.6	30.7	35.4	39.6
36 h Ball milling	17	32.3	39.9	43.4
Roll milling	18	32.8	40.8	45.4
<u>35% cement replacement</u>				
Hammer milling	12.7	17.4	21.6	28.8
24 h Ball milling	14.3	27.4	29.2	38.7
36 h Ball milling	14.9	30.1	33.3	42.6
Roll milling	16.3	30.9	35.6	43.3
<u>40% cement replacement</u>				
Hammer milling	11	15.9	21	27.9
24 h Ball milling	12.2	20	27.3	36.4
36 h Ball milling	13.2	20.4	30.5	40.5
Roll milling	14.6	22.4	32.1	41.3
<u>50% cement replacement</u>				
Hammer milling	8	14.9	20.6	27.1
24 h Ball milling	9.9	18.3	23.9	36.5
36 h Ball milling	10.3	19.3	24.4	39
Roll milling	11.2	18.8	25.4	40.1

(Source: Sarfo-Ansah, 2010)

The compressive strength of the Mfensi pozzolana cement mortar cubes were lower than that of ordinary Portland cement mortar cubes at all cement replacement levels. However, except for the hammer milled pozzolana, they satisfied the ASTM, EN, and Ghana standards.

Sarfo-Ansah (2010) also investigated the effect of mechanical activation on standard consistency, initial and final setting times of Mfensi clay pozzolana. Sarfo-Ansah in his

studies (Table 2.7) found that, the standard consistence (or water requirement) of the Mfensi pozzolana cement pastes increased steadily as the pozzolana content of the paste increased for all types of grinding.

Table 2.7: Setting times and standard consistency for Mfensi pozzolana

Milling type and period	Setting time, min		Standard consistency, %
	Initial	Final	
0% replacement (control)	185	280	28.2
30% cement replacement			
Hammer milling	135	251	40.6
24 h ball milling	123	240	43.0
36 h ball milling	110	237	47.6
Roll milling	98	228	47.8
35% cement replacement			
Hammer milling	112	246	44.6
24 h ball milling	86	230	47.4
36 h ball milling	70	225	49.2
Roll milling	64	219	50.1
40% cement replacement			
Hammer milling	87	240	46.4
24 h ball milling	64	218	48.2
36 h ball milling	60	207	52.6
Roll milling	56	198	53.5
50% cement replacement			
Hammer milling	79	225	48.0
24 h ball milling	61	168	52.0
36 h ball milling	50	155	57.2
Roll milling	48	142	58.2

(Source: Sarfo-Ansah, 2010)

The standard consistence also increased with increasing fineness. Thus, the lowest standard consistence was obtained for hammer milling whilst the highest was recorded for

roll milling. OPC paste had a standard consistence of 28.2% which increased to 58.2% when 50% of it was replaced by the roll mill product. This behavior can be explained by the fact that decreasing the particle size during milling results in a lower bulk density of the powdered pozzolana. This implies that larger volumes would be required to replace an equal mass of OPC, therefore the amount of water needed to get a workable paste also increased.

Initial setting times decreased significantly as pozzolana content in the blended cements increased. The decrease was pronounced for all milled products. This was because at such high fineness levels the pozzolana reacted faster with the ordinary Portland cement leading to faster setting (Sarfo-Ansah, 2010). Above 30% replacement, the activated pozzolana cements set faster than the EN 197-1 minimum standard of 75 min. However, they all set well above the ASTM C 595 minimum standard of 45 min.

Final setting times for all degrees of milling decreased with increasing pozzolana content. All the Mfensi pozzolana samples attained final sets below 5 h which satisfied both the EN 197-1 and ASTM C 595 maximum standards of 600 min (10 h) and 420 min (7 h) respectively as is shown in Table 2.7. As the pozzolana content of the pastes increased, the final setting times decreased for all the different types of milling. For a particular pozzolana content of the paste, the coarser pozzolana obtained by hammer milling had the highest final setting time and the finest sample obtained by roll milling gave the lowest final setting time.

2.4.3 Chemical activation

In chemical activation, either the pozzolanic material is treated with a chemical compound solution before it is added to the concrete or the chemical as a separate ingredient is directly put into the concrete containing natural pozzolana (Aldemir, 2006). Use of chemical activators changes hydration products and accelerates pozzolanic reaction, which leads to faster strength developments and higher ultimate strength. Although the addition of activators increases the cost of raw materials, the cost per unit strength increases. In chemical activation, the activators can be added during the grinding of the pozzolana or the mixing of mortar or concrete mixtures. The requirement for additional equipment and modifications are very minimal (Shi and Day, 2001). Based on strength development and cost per unit of strength increase, addition of chemical compounds is the most economical and effective activation method. It is also the most feasible one among the other methods due to its ease of application (Aldemir, 2006).

Numerous investigators have utilised chemical activation to activate fly ash systems. Two different methods commonly utilised include alkali activation and sulfate activation (Owens et al, 2010). Alkali activation involves the breaking down of the glass phases in an elevated alkaline environment to accelerate the reaction (Shi, 1998). Sulfate activation is based on the ability of sulfates to react with aluminium oxide in the glass phase of fly ash to form sulfates (AFt) that contributes to strength at early ages (Xu & Sarkar, 1991; Shi, 1996; Shi, 1998). The possibility of fly ash activation mainly lies in the breaking down of its glassy phases. Fraay (1989) considered that the pH value required to dissolve the alumina and silica is about 13.3 or higher. The usual way of achieving a high pH is by

the addition of NaOH or other alkaline materials into the fly ash system. Studies carried out by Shi and Day (1996 & 1998) compared the addition of Na_2SO_4 and CaCl_2 and found that the addition of both increased the cost of raw materials but the cost per unit strength decreased. The addition of 4% Na_2SO_4 increased both the early and later age strength of paste systems whereas the addition of 4% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ lowered the early age strength but increased the later strength. Poon (2001) used an addition of 10% of anhydrite to activate a mortar system incorporating 55% fly ash and found that 3 day strengths were improved by about 70%. It also increased the strength at later ages of these mortars.

Another method commonly used by industry to improve early age strengths is to use chemical admixtures. Many commonly available admixtures have the potential to accelerate the hydration of Portland cement systems, whilst also being high range water reducers and superplasticiser at the same time. The reduction of free water in the pastes due to the addition of a superplasticiser can result in improved strengths (Neville, 2002).

The use of chemical compounds has been very effective in activation of potential cementitious property of blast furnace slag and pozzolanic reactivity of pozzolanas. Shi and his colleagues have conducted a series of studies on the chemical activation of reactivity of coal fly ashes. Figure 2.6 shows the addition of 3% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ on the strength of the blended cement mortars containing 50 and 70% coal fly ash. At 50% replacement level, the strength of the blended cement was increased by approximately 50% at 7 days, and by approximately 70% at 28 days and approximately

60% at 56 days. As fly ash replacement is increased from 50% to 70%, the addition of 3% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ increased the strength of the blended cement by approximately 100% at 7 days, 62% at 28 days and 67% at 56 days. One interesting fact is that the cement containing 70% coal fly ash and 3% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ showed higher strength than the cement containing 50% coal fly ash at 28 and 56 days. This means that the use of CaCl_2 is very effective to increase the strength of the blended cement mortars.

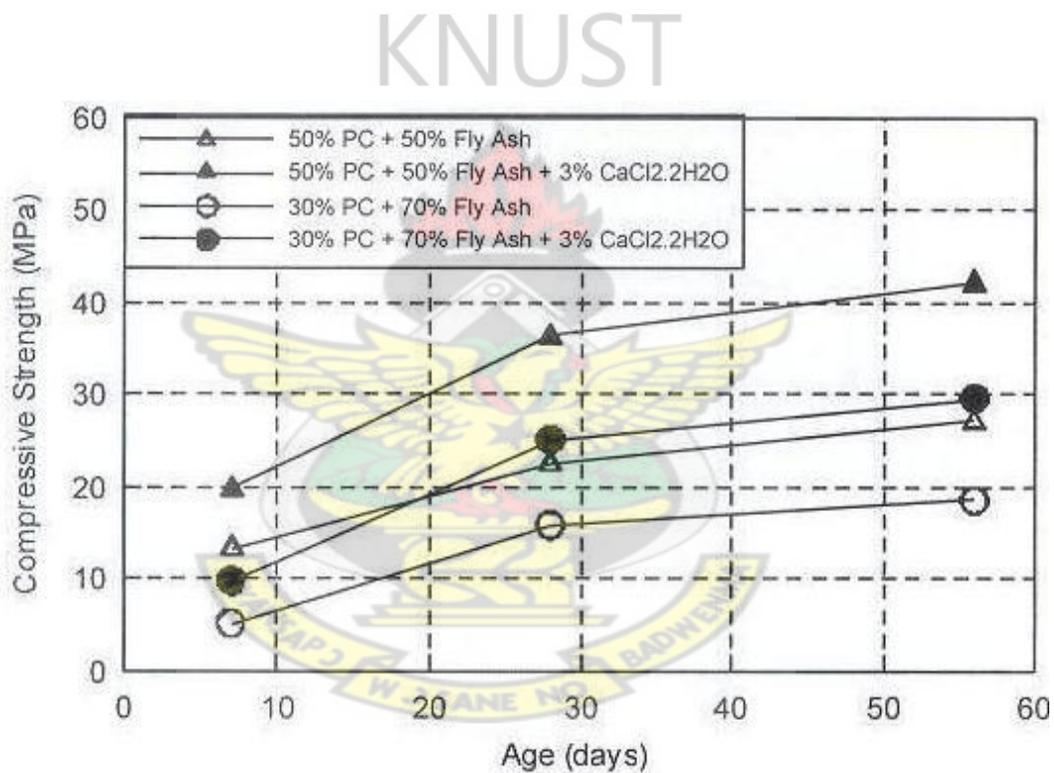


Figure 2.6: Effect of CaCl_2 on strength development of blended cement mortars containing high volume fly ash. (Source: Shi, 2001)

Figure 2.7 shows the addition of 3% Na_2SO_4 on the strength of the blended cement mortars containing 30 and 70% coal fly ash. When 30% cement is replaced with coal fly ash, the addition of 3% Na_2SO_4 increases strength by approximately 40%

from 3 to 28 days. However, as fly ash replacement level is increased from 30 to 70%, the addition of 3% Na₂SO₄ increases strength by approximately 80% from 3 to 28 days. This means that the use of Na₂SO₄ is particularly effective with high fly ash replacement. Shi and Day (2001) examined the pozzolanic reaction mechanisms in the presence of CaCl₂ and Na₂SO₄.

The activation mechanisms can be briefly summarized as follows. The introduction of CaCl₂ decreases the solubility of Ca(OH)₂ and the pH of pore solution due to the common ion effect which decreases the dissolution of fly ash but favors the formation of a solid solution of Ca₄Al₂[(SO₄²⁻)_X(Cl⁻)_Y(OH)_{2-2X-Y}].nH₂O (X<1 and Y<2). The formation of the solid solution speeds up the dissolution of fly ash particles and the pozzolanic reaction, which enhances the strength of fly ash cement and concrete. The addition of Na₂SO₄ to fly ash cement increases the alkalinity of the solution and the dissolution of fly ash during initial stages, and accelerates the pozzolanic reaction between lime and fly ash. Also it results in the formation of more ettringite, which results in a significant solid volume increase, a less porous structure and higher strength.

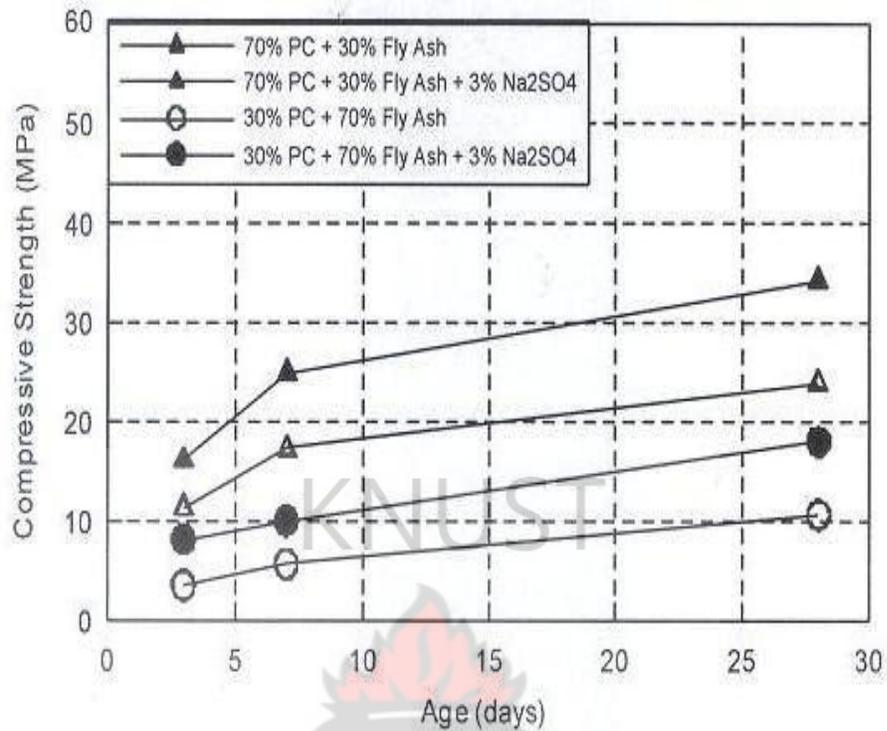


Figure 2.7: Effect of Na₂SO₄ on strength development of blended cement mortars containing high volume fly ash. (Source: Qian, 2001)

2.4.3.1 Effect of chemical activators on setting times

Activated pozzolana is either done to increase the rate of early strength development or to shorten the times of setting, or both. Allahverdi and Ghorbani (2006) studied the effect of chemical activators on the setting behavior of the lime-natural pozzolana cement. Figure 2.8 and 2.9 shows initial and final setting times of the studied lime-natural pozzolana cement without and with chemical admixtures at different dosages of 2, 4, and 6 % by weight respectively. The initial and final setting times of the lime-natural pozzolana cement without chemical admixture were 37 and 54 hours respectively at an atmosphere of more than 95% relative humidity and at 25°C.

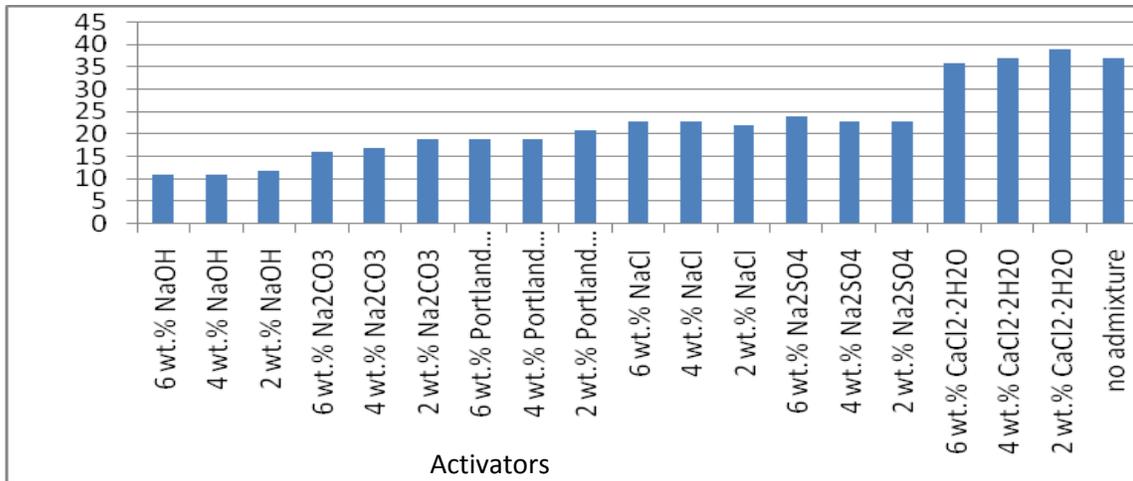


Figure 2.8: Initial setting time of the studied lime-natural pozzolana cement without and with chemical activators (h)

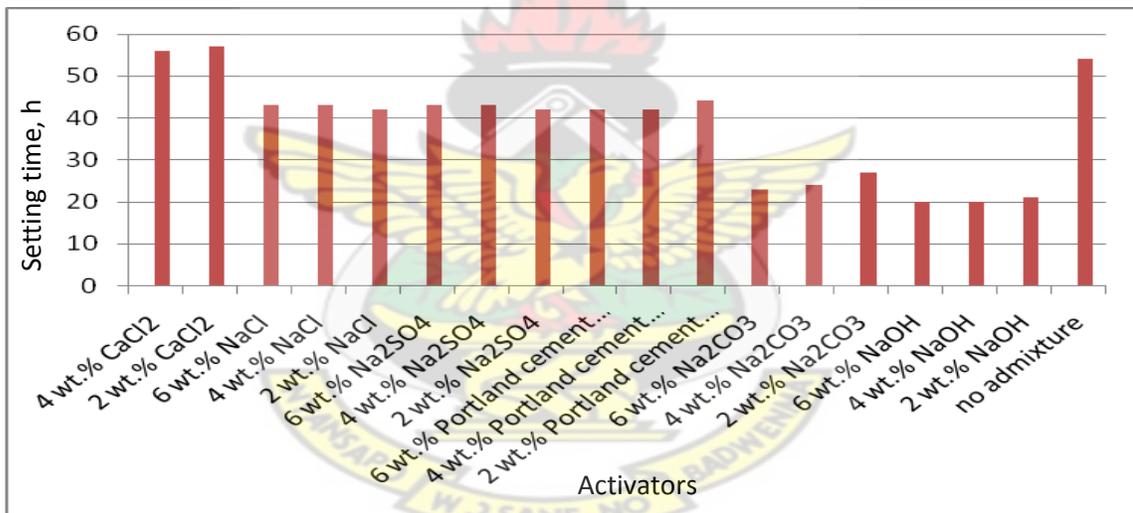


Figure 2.9: Final setting time of the studied lime-natural pozzolana cement without and with chemical activators (h). (Source: Allahverdi and Ghorbani, 2006)

From Figure 2.9, all the used chemical admixtures were effective and could more or less decrease both initial and final setting times, except calcium chloride. Sodium hydroxide however was the most effective set accelerator. Addition of 4% NaOH decreased the initial and final setting times of the lime-natural pozzolana cement to 11 and 20 hours

respectively.

2.4.3.2 X-ray diffraction (XRD) of chemically activated mortar paste

Allahverd and Ghorban (2006) also studied the crystalline mineral phases of a 50-day hardened paste of pozzolana cement containing 6 wt.% Na_2SO_4 using X-ray diffractometry technique. The X-ray diffraction patterns of the hardened paste of lime-natural pozzolana cement, and hardened paste of lime-natural pozzolana cement containing 6 wt.% Na_2SO_4 are presented in Figures 2.10 and 2.11. The crystalline mineral phases identified were hardened paste of lime-natural pozzolana cement; Portlandite ($\text{Ca}(\text{OH})_2$), Actinolite ($\text{Ca}_2\text{Mg}_3\text{Si}_8\text{O}_{22}(\text{OH})_2\text{Fe}_2^{2+}$), Anorthite and hardened paste of lime-natural pozzolana cement containing 6 wt.% Na_2SO_4 : Albite ($\text{Na}_{0.95}\text{Ca}_{0.05}\text{Al}_{1.05}\text{Si}_{2.95}\text{O}_8$), Portlandite and Actinolite.

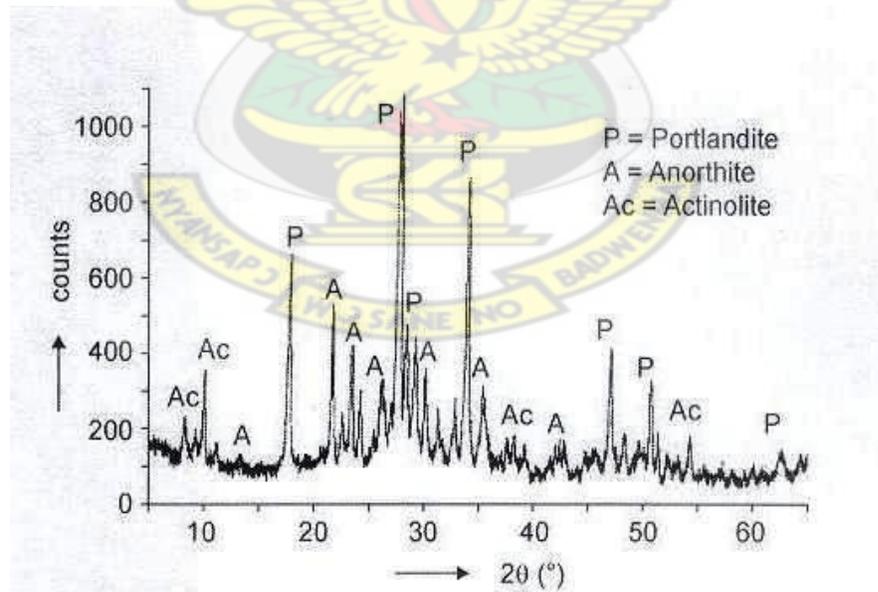


Figure 2.10: X-ray diffraction pattern of the 50-day hardened paste of lime-natural pozzolana cement without any chemical admixture. (Source: Allahverd and Ghorban, 2006)

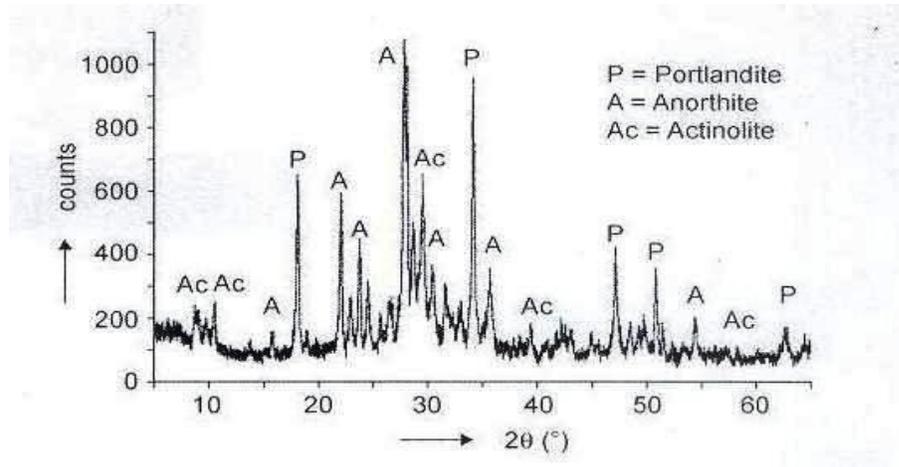


Figure 2.11: X-ray diffraction pattern of the 50-day hardened paste of lime-natural pozzolana cement containing 6 wt.% Na_2SO_4 . (Source: Allahverd and Ghorban, 2006)

According to the results obtained, both hardened pastes of lime natural pozzolana cement without and with chemical admixture have the same crystalline mineral phases except the two phases Anorthite and Albite. These two phases belong to the feldspar group of minerals and possess almost the same properties, so that such a difference in the crystalline phases of the two cement systems is less probable to be responsible for the difference observed in their strength and setting behaviors. Knowing that the compressive behavior of the lime-natural pozzolana material is mainly due to formation of gel-like C–S–H type hydrates, the compressive strength improvement with addition of 6 wt.% Na_2SO_4 therefore is due to higher contents of amorphous C–S–H gels and/or less probably different amorphous binding phases not detectable by X-ray diffractometry.

2.4.3.3 Scanning electron microscopy (SEM) of chemically activated mortar paste

Allahverd and Ghorban (2006) again studied the morphology of the microstructures of the two 50-day hardened pastes without any chemical admixture and with 6 wt.% Na_2SO_4 with a scanning electron microscope. Figures 2.12 and 2.13 show SEM-images taken from the microstructure of the two hardened pastes without any chemical admixture and with 6 wt.% Na_2SO_4 respectively. Observations by SEM revealed that the microstructure of the two hardened pastes were quite similar. They consisted of mostly amorphous phases along with few microcrystalline phases observable only at relatively high magnifications. EDAX analysis using ZAF-correction clearly confirmed the presence of relatively large Portlandite crystals accumulated around small voids in both hardened pastes. Figure 2.13 shows a number of relatively large Portlandite crystals precipitated around a small void in microstructure of the 50-day hardened paste of lime-natural pozzolana cement with 6 wt.% Na_2SO_4 .

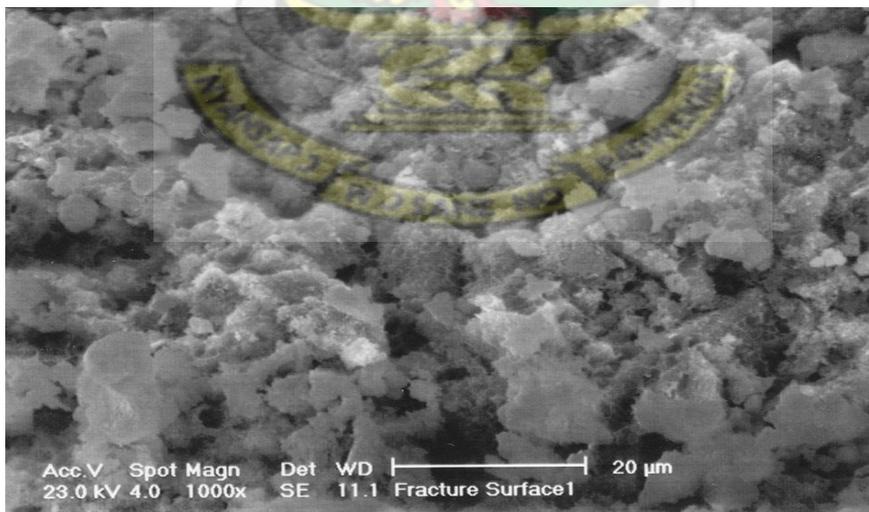


Figure 2.12: SEM-image of the microstructure of 50-day hardened paste of lime-natural pozzolana cement without any chemical admixture.

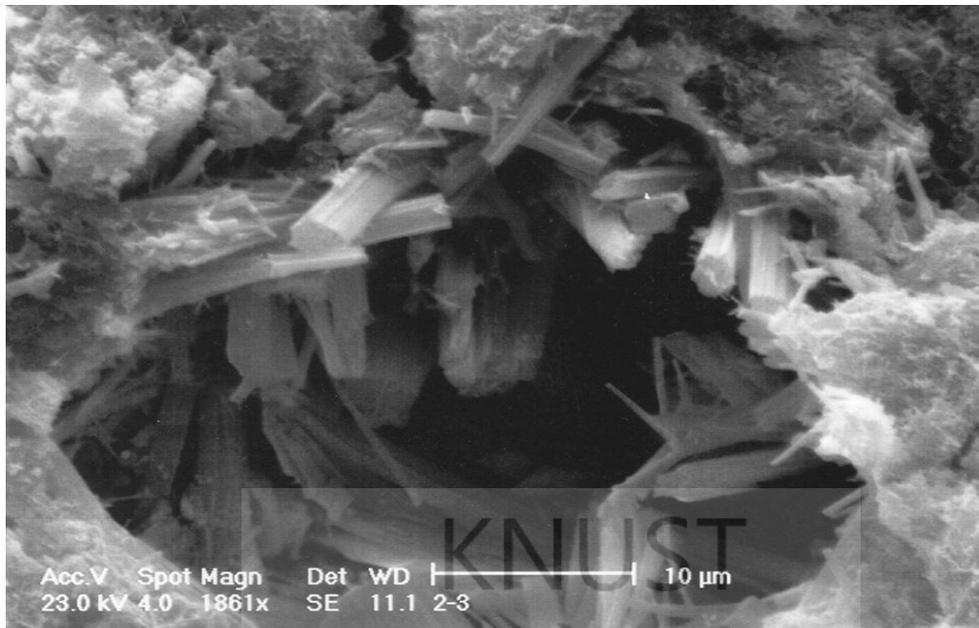


Figure 2.13: SEM-image of the microstructure of 50-day hardened paste of lime-natural pozzolana cement containing 6 wt.% Na_2SO_4 .

(Source: Allahverd and Ghorban, 2006)

2.5 Advantages of chemical activators

Activators confer several beneficial effects on concrete including reduction in water requirement, increased workability, controlled setting, accelerated hardening, improved strength, better durability, desired coloration and volume changes (Ramachandran, 1995). Many inorganic compounds play this role, including chlorides, fluorides, carbonates, nitrites, thiosulfates among others. Organic compounds such as triethanolamine, diethanolamine, propionate, urea, glyoxal, and formate have also been advocated for use as activators. The use of activators is generally based on trial-and-error because of an incomplete understanding of their mechanism of action. One approach is to study the interactions that occur between the activators and the hydrating cement components. The activators may remain in a free state as a solid or solution may interact at the surface or

chemically combine with the constituents of cement or cement paste. The type and extent of interaction may influence the physico-chemical and mechanical properties of concrete such as water demand, hydration kinetics, composition of the products, setting times, microstructure, strength, and durability (Ramachandran, 1995).

The advantages of accelerators (activators) include; efficient start and finishing operations, reducing the period of curing and protection, earlier removal of forms so that the construction is ready for early service, plugging of leaks, and quick setting when used in shotcreting operations (Ramachandran, 1995).

The American Concrete Institute Committee 212 (1990) has divided accelerators into four groups as follows:

- i. Soluble inorganic salts that include chlorides, bromides, fluorides, carbonates, thiocyanates, nitrites, nitrates, thiosulfates, silicates, aluminates and alkali hydroxides that accelerate the setting of Portland cement;
- ii. Soluble organic compounds such as triethanolamine (TEA), calcium formate, calcium acetate, calcium propionate, and calcium butyrate. The other two groups are used in combination with water reducers:
- iii. Quick setting admixtures used in shotcrete applications and which promote setting in few minutes and may contain sodium silicate, sodium aluminate, aluminium chloride, sodium fluoride, strong alkalis and calcium chloride; and
- iv. Miscellaneous solid admixtures such as calcium aluminate, seeds of finely divided Portland cement, silicate minerals, finely divided magnesium carbonate and

calcium carbonate.

2.5.1 The effect of chemical activators on concrete and mortar paste

2.5.1.1 Rheological effects

Most admixtures do not significantly alter the rheology of cement pastes at early ages. The quicker stiffening of accelerated pastes will, of course, result in higher viscosities at a later age. More complex formulations occasionally include water-reducing admixtures to reduce the water-cement ratio, and their effect will be a function of the water-reducing admixture type and content.

2.5.1.2 Effects on heat evolution

The heat evolution of concrete mixes containing no admixture, 1.5% calcium chloride and 3.0% calcium formate as shown in Figure 2.14.

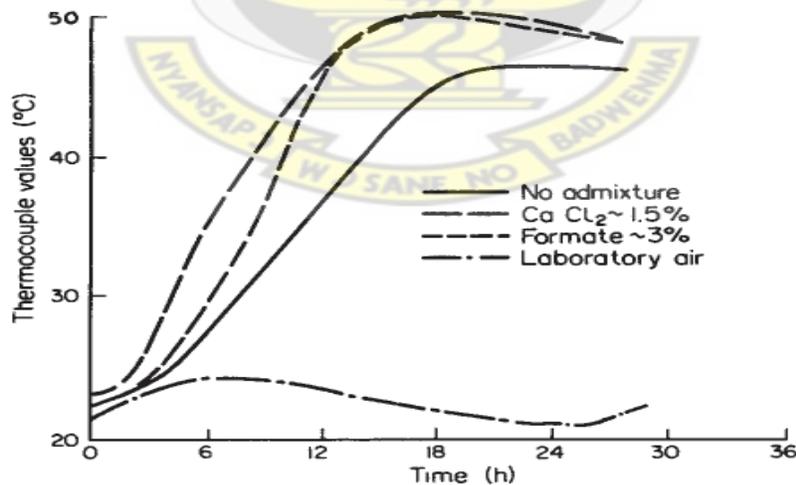


Figure 2.14: Heat evolution of insulated concrete cube containing calcium chloride and calcium formate. (Source: Rixom and Mailvaganam, 1999)

2.5.1.3 Effect on permeability

The permeability and porosity of concrete containing calcium chloride in relation to a plain concrete depends on two conflicting variables:

i. The degree of hydration of the concrete, which in the case of the calcium chloride-containing concrete will initially be considerably increased, and the larger volume of hydration products will lead to a reduced permeability.

ii. The adverse effect that calcium chloride has on the capillary porosity distribution.

At later ages (after perhaps 1 year) the degree of hydration in both calcium chloride-containing concrete and a plain concrete will be similar and, under these circumstances, the concrete will be more porous and allow easier access to aggressive gases and liquids. Pore volume distributions of cement pastes at an advanced state of hydration of more than 90% (Rixom and Mailvaganam, 1999) are shown in Figure 2.16, where the greater porosity is indicated and the data can be used to calculate an increase in average hydraulic radius from 28 Å (2.8 nm) in the chloride-free sample, to 108 Å (10.8 nm) in the chloride-containing sample.

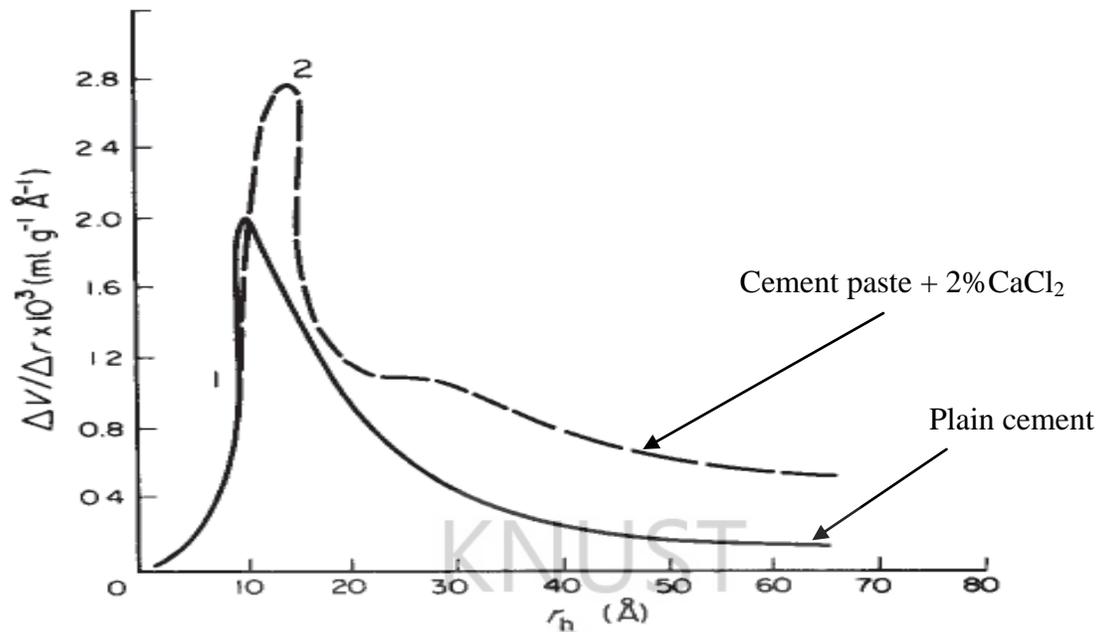


Figure 2.15: Pore volume distribution of cement pastes from nitrogen adsorption. (Source: Rixom and Mailvaganam, 1999)

2.5.1.4 Resistance to sulphate attack

Calcium chloride contributes to a lower resistance of concrete to sulfate attack. In Type I, 11, and V concretes containing different amounts of cement, 2% calcium chloride increased sulfate expansion (Ramachandran, 1995). Compressive strengths are also decreased. The sulfate resistance of concrete containing CaCl_2 is decreased to a greater extent when it has lower cement contents. The detrimental effect of calcium chloride can be counteracted to some extent by using air entrained concrete. The expansion of concrete in the presence of CaCl_2 may be due to several reasons. Small expansion may be due to the formation of $\text{CS}(\text{HC1})$ compound (Kalousek et. al, 2000). The calcium chloroaluminate may favor the growth of calcium sulfoaluminate crystals. Ben Yair (2001) found that in the presence of CaCl_2 , sulfoaluminate needles grew from 60 microns to 300

microns in length. In a re-examination of the effect of CaCl_2 on sulfate resistance of concrete, Harrison (1990) exposed concrete containing different amounts of chloride to a $\text{Na}_2\text{SO}_4\text{-MgSO}_4$ solution. The specimens were initially cured for 28 days. Mean compressive strengths after 7 years of immersion showed that even at 4% CaCl_2 , little or no enhanced effect of sulfate attack occurred. The amount was found to be 0.4% chloride below which increased sulfate attack occurred.

2.5.1.5 Effect on shrinkage

The drying shrinkage of concrete containing calcium chloride is increased in comparison to plain concrete, even though the amount of moisture lost is less (Rixom and Mailvaganam, 1999). This is illustrated in Fig. 2.16 and it is thought that the reduced moisture loss will be due to the more advanced state of hydration in the specimens containing calcium chloride. The increased shrinkage must, therefore, be a characteristic of the type of cement hydration products formed. Under saturated conditions, such as total water immersion, the amount of expansion of the concrete is reduced when calcium chloride is present. There are only limited data available on the effect of other accelerating admixtures, although one comparative study by Bruere et. al (1971) suggests that calcium formate and triethanolamine also increase the drying shrinkage of concrete into which they are incorporated.

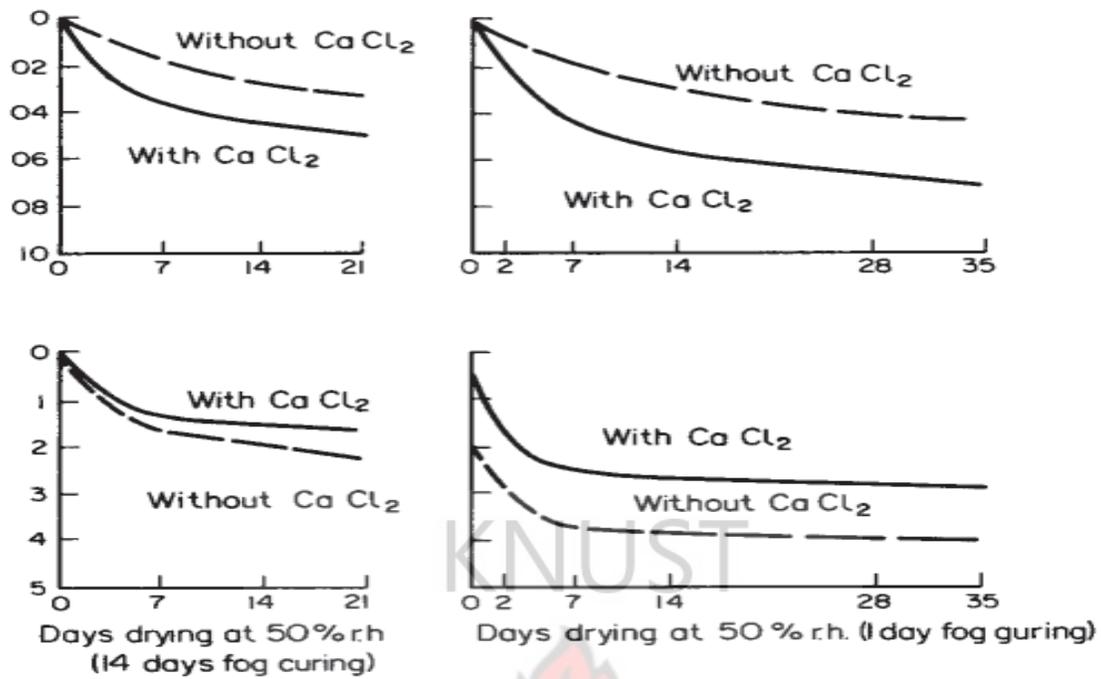


Figure 2.16: CaCl₂ increases drying shrinkage of concrete, although the moisture content is decreased. (Source: Rixom and Mailvaganam, 1999)

2.5.1.6 Effect on workability

It is generally observed that addition of CaCl₂ increases slightly the workability and reduces the water required to produce a given slump of concrete. In combination with an air-entraining agent, CaCl₂ may sometimes improve further the workability. A small increase in air content and average size of air voids may also result (Ramachandran, 1995).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The materials used for this study include: ordinary Portland Cement (OPC), clay pozzolana, chemical activators and river sand, which were all obtained from various places in Ghana.

3.1.1 Ordinary Portland cement (OPC)

Ordinary Portland cement of class 42.5N (according to EN 197- 1) manufactured by Ghacem, a subsidiary of Heidelberg Cement was used for the preparation of the mortar and paste specimens.

3.1.2 River sand

Ordinary river sand from Fumesua, near Kumasi was used for the mortar mixes and satisfied the BS 4550: Part 6 requirements. The sand was sieved passing through 0.85mm test sieve and retained on 0.60mm test sieve.

3.1.3 Clay pozzolana

The clay pozzolana used in this work was obtained from CSIR-BRRI, pozzolana factory, at Fumesua. The obtained pozzolana was firstly characterized for its chemical and physical compositions.

3.1.4 Activators

Calcium chloride (CaCl_2), sodium sulphate (Na_2SO_4) and aluminium chloride (AlCl_3) were used as activators in this study.

3.2 Methods

3.2.1 Physical Properties

The following physical properties of the materials (OPC, sand, pozzolana) were determined:

- Particle size distribution
- Specific gravity
- Blaine fineness

3.2.1.1 Particle size distribution

The particle size distribution of the pozzolana cement samples were determined by the hydrometer method of sedimentation as specified by British Standard BS 1377:90. 200g of the samples were dried in an oven at 105°C for 4hrs. The dry samples were then quartered and 50g of each sample was transferred into a 600ml brass container. 100ml of a dispersant solution, made from 7g of sodium metahexaphosphate ($\text{Na}_6\text{P}_6\text{O}_{19}$) and 33g of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) dissolved in 1 litre of distilled water, was added to each sample and made up to 250ml with distilled water.

The suspensions were agitated with a mechanised stirrer for 15 minutes and each sample was later transferred to a 1 litre measuring cylinder. The contents were made up to 1 litre

with distilled water and left to stand undisturbed for 24hrs to effect the decoagulation of the various particles. The cylinder was agitated manually by holding the measuring cylinder containing the suspension between the palms and turning it upside-down for a minute to disperse the particles and placed on a bench. The timer was immediately switched on. The hydrometer readings were first taken after 30secs and then after 1, 2 and 4mins and specific intervals for 8hrs and at 24hrs. After the hydrometer readings, the samples were washed through a 75 μm sieve and the material retained, if any, was dried at 105°C for 24hrs. The dry samples were passed through 0.6, 0.4 and 0.2 mm, 150 and 75 μm standard sieves and the retained on each sieve recorded.

3.2.1.2 Specific gravity

The specific gravity of the test sample was determined as specified by the British Standard BS 1377:90. A 50ml density bottle with the stopper on was dried in an oven and weighed (m_1). 25g of the pozzolana cement sample was oven-dried at 105°C for 24 hours. The sample was transferred into the density bottle and the bottle with its contents and the stopper weighed again as (m_2). Then the sample in the bottle was covered with kerosene of known specific gravity. With the stopper removed, the container was placed in a vacuum desiccator, and the air gradually evacuated. When no air was seen to be released, the bottle was removed from the desiccator and filled with de-aired kerosene. The stopper was again inserted and the bottle immersed in a water bath until a constant temperature of 25°C was attained. The bottle was then wiped dry and weighed (m_3). The bottle was afterwards emptied of its contents, cleaned and completely filled with kerosene, stoppered and reweighed (m_4).

The specific gravity (G_s) of the sample was calculated as:

$$G_s = \frac{G_L(m_2 - m_1)}{(m_4 - m_1) - (m_3 - m_2)}$$

where G_L = specific gravity of kerosene. 3.1

3.2.1.3 Blaine fineness

The Blaine indices of the pozzolana cement samples were determined with an air permeability apparatus at the laboratories of Ghacem Ltd according to methods outlined by 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 2.715g of the sample to be tested 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 marks determined in seconds.

3.2.2 Chemical analysis

The chemical analysis of the pozzolana cement samples was determined using the X-ray fluorescence equipment (Spectro X-lab) at the Geological Survey Department in Accra. 4g of each sample was mixed with 0.09g of wax and then milled in a milling machine for 3 minutes to produce a homogeneous mixture. The 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 for irradiation and finally to determine the chemical composition of the samples.

3.2.3 X-ray diffraction analysis

The PHILIPS PW 1830 X-ray diffractometer at the Materials Science Department Laboratory of the University of Manchester, United Kingdom, was used to analyze the OPC and pozzolana samples used for this work. 0.5g of the powdered samples were prepared by compressing them into pellets which were labelled and placed in the X-ray diffractometer for analysis. The samples were analyzed between an angle of 5° to 55° (2θ) using the Cu K alpha radiation. The voltage and current of the X-ray tube were set at 40KV and 40mA respectively.

3.2.4 Engineering Properties

3.2.4.1 Compressive strength

The tests for the determination of the compressive strength of the pozzolana cement mortar cubes were carried out according to methods specified by the European Standard EN 196-1:2000. The clay pozzolana was blended with ordinary Portland cement using cement replacement of 10, 20, 30 and 40% by mass. River sand was used to prepare mortar cubes for the compressive strength determination. The sand satisfied the requirements of the European Standard EN 196-2:2000.

Pozzolana cement to sand ratio of 1:3, water to pozzolana cement ratio of 0.5 for all levels of Portland cement replacement were used to prepare the mortar test cubes. The same 1:3

water to cement ratio was used to produce the control cubes using only ordinary Portland cement.

The materials for each mortar cube were mixed separately. The pozzolana and the cement were mixed first in a motorized mixer and then mixed with the measured quantity of sand. Afterwards, the required quantity of water, containing the chemical compound (activator), was added and mixed for about 4 min.

The mortar cubes were moulded in 70×70mm metal moulds at an average room temperature of 27°C. The moulding involved tamping the mortar in the moulds and then vibrating them on a vibrating machine for 2 minutes. After gauging, the moulds were covered with a metal plate and placed under damp jute sacks to be cured for 24 hours. The pozzolana cement cubes were removed from their moulds after 24 hr and immersed in a pond of water of average temperature of 22°C and kept for the specified curing periods of 2, 7, 28 days. The cubes after curing were tested for compressive strength by loading the sides of the cubes uniformly with a compressive strength testing machine until fracture appeared. The maximum load in KN at which fracture occurred was recorded and used to calculate the compressive strength as

$$R_c = \frac{1000F_c}{A_r} \quad 3.2$$

Where

R_c = compressive strength, MPa

F_c = maximum load at which fracture occurs, KN

A_r = area of a face of the cube, mm²

For each crushing test 3 cubes were used and the average was taken for the compressive strength.



Figure 3.1: Compressive strength testing machine

3.2.4.2 Standard consistency (Water demand)

The Vicat method as specified by the European Standards EN 196-3:2000 was used to determine the standard consistency of both pozzolana and ordinary Portland cement pastes. In this method a measured quantity of the cement is gauged with water (containing the activator) until the resistance to penetration of a plunger reached a specified level. The ratio of the water required to the weight of cement and expressed as a percentage is taken as the standard consistency of the cement. The plunger, made of brass, is of at least 45 mm effective length and 10 mm diameter. The Vicat mould, also made of brass, is in the form of a truncated cone with a depth of 40 mm and an internal diameter of 75 mm.

The Vicat mould, resting on a non-porous plate, was filled completely with the cement paste in one layer and the surface smoothed off level with the top of the mould as quickly as possible.

The test block, confined in the mould and resting on the plate was placed under the rod bearing the plunger. The plunger was lowered gently into contact with the surface of the test block and quickly released and allowed to sink in.

Trial cement pastes, made with varying amounts of water, containing the chemical activator, were used until the plunger penetrated a distance of not more than 5mm from the bottom of the mould. The amount of water used was recorded and expressed as a percentage by mass of the dry pozzolana cement to give the standard consistency of the pozzolana cement.

3.2.4.3 Setting time

3.2.4.3.1 *Initial setting time*

The Vicat method was also used for the determination of the initial setting time. The pozzolana cement paste, using the percentage of water recorded for the standard consistency, was gauged into the Vicat mould. The paste, confined in the mould and resting on the base plate, was placed under the Vicat apparatus with the needle provided for the initial setting time determination in place. The needle was then lowered gently into contact with the surface of the test block and quickly released and allowed to sink in. This process was repeated until the needle, when brought into contact with the test block and

released as described above, did not penetrate beyond a point approximately 4 mm from the bottom of the mould. The period elapsing between the time when the water was added to the cement and the time at which the needle ceased to pierce beyond 4 mm from the bottom of the test block was noted as the initial setting time.

3.2.4.3.2 *Final setting time*

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



Figure 3.2: Vicat apparatus with plunger and Vicat needles

3.2.4.4 Water Permeability

The water permeability was determined by water absorption which measures the pore spaces indirectly by the procedure given in ASTM C642-90. For this test, 70×70mm mortar cubes were cast, cured and demoulded after 24 hours. After demoulding, the specimens were kept immersed in water. The test was conducted at the end of 28 days to evaluate the effect of chemical activators on overall porosity. At the end of 28 days, the specimens were taken from the curing tank and air-dried to remove surface moisture. After this, the specimens were dried in an oven at a temperature of 100 ± 10 °C for 48 hours, allowed to cool at room temperature, and the weight of the specimens measured to an accuracy of 1g using a digital balance. The specimens were then kept immersed in water for 1 hour and increase in weight was measured. From this the co-efficient of water absorption was calculated using the following formula:

$$K\alpha = \frac{[Q/A]^2}{t} \quad 3.3$$

Where

$K\alpha$ – the co-efficient of water absorption ($\text{Kg}^2/\text{m}^2/\text{s}$).

Q – the quantity of water absorbed by the oven-dry specimen (kg) in time, t (s).

A – the total surface area of concrete specimen through which water penetrates (m^2).

CHAPTER FOUR

TEST RESULTS AND DISCUSSION

4.1 Physical Properties

The specific gravities and Blaine indices of the OPC, clay pozzolana and the various percentage replacements of pozzolana cement used in this study have been presented in Table 4.1 below.

Table 4.1: Specific gravities and Blaine fineness of OPC, clay pozzolana and pozzolana cement of different percentage replacement.

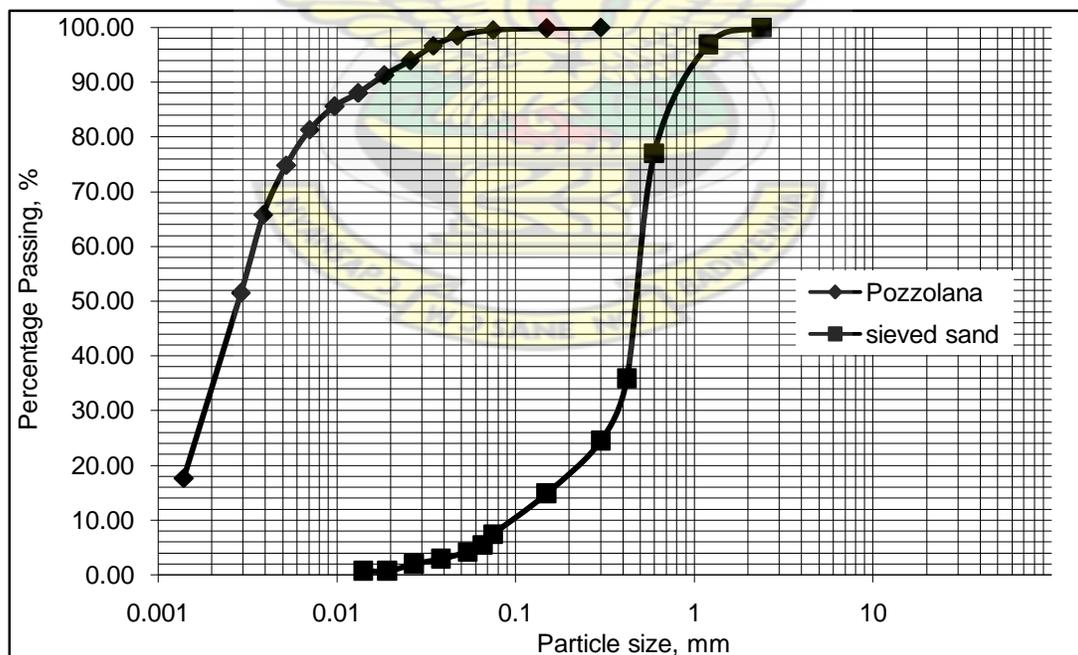
Sample	Specific gravity	Blaine fineness, m ² /Kg
OPC	3.18	338
Clay pozzolana	2.67	442
10% pozzolana cement	3.03	388
20% pozzolana cement	2.97	410
30% pozzolana cement	2.92	420
40% pozzolana cement	2.82	432

It is seen from Table 4.1 that ordinary Portland cement (OPC) recorded the highest specific gravity of 3.18 whereas clay pozzolana recorded the least value of 2.67. It is observed that specific gravity of the pozzolana cement decreased as the pozzolana content in the cement increased ranging from 3.03 to 2.82. On the other hand, OPC obtained the least Blaine

index of $338\text{m}^2/\text{kg}$ whereas clay pozzolana recorded the highest of $442\text{m}^2/\text{kg}$. Also, the Blaine indices of pozzolana cement increased as pozzolana content increased from 10 to 40%. This indicates that the surface area of the mix increased as the pozzolana content increased.

4.1.1 Particle size distribution

Figure 4.1 represents the particle size distribution of the pozzolana and sieved sand used for this study. The figure shows that about 85.6% of the pozzolana particles are finer than $100\mu\text{m}$. The sieved sand on the other hand contains about 95.5% sand and 4.5% silt. This is an indication that the sand used was very coarse and contained minimal amount of silt.



4.2 Chemical Composition

The results of the chemical analysis of OPC, clay pozzolana and pozzolana cements as determined by X-ray fluorescence (XRF) have been presented in Table 4.2.

Table 4.2: Chemical composition of OPC and pozzolana cement samples

Constituents, %	Clay					
	OPC	Pozzolana	P ₁₀	P ₂₀	P ₃₀	P ₄₀
SiO ₂	18.88	62.77	18.37	16.53	15.07	19.05
Al ₂ O ₃	3.57	18.71	2.65	4.93	4.58	4.13
Fe ₂ O ₃	3.36	11.68	4.46	3.07	2.66	4.41
CaO	59.64	0.25	59.18	58.44	58.8	55.01
MgO	1.89	1.46	1.54	2.64	3.98	1.44
MnO	0.14	0.46	0.2	0.06	0.04	0.1
TiO ₂	0.14	0.41	0.09	0	0.34	0.32
SO ₃	4.93	0.19	3.29	3.06	3.23	3.44
Na ₂ O	4.7	0.21	0.15	0.09	0.24	0.12
P ₂ O ₅	0.22	0.03	0.03	0.01	0.01	0.04
Cl	0.01	0	0.01	0	0.01	0
K ₂ O	2.12	1.08	0.55	0.66	0.62	0.72
L.O.I	3	2.75	9.5	10.5	11.1	12

P₁₀ – OPC with 10% pozzolana content; P₂₀ – OPC with 20% pozzolana content

P₃₀ – OPC with 30% pozzolana content; P₄₀ – OPC with 40% pozzolana content

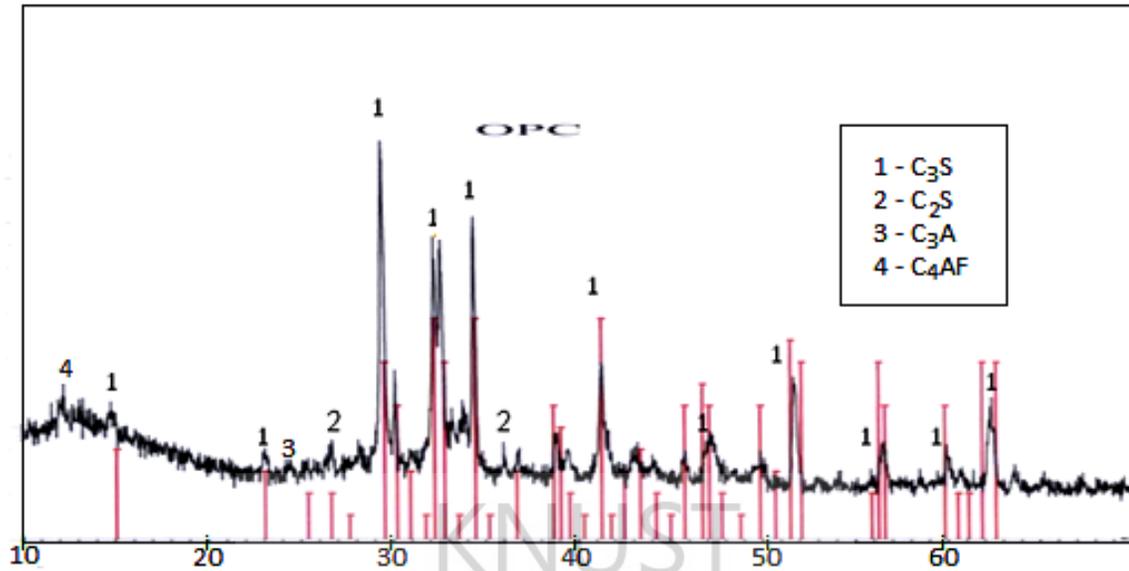
From Table 4.2, the OPC had a CaO and SiO₂ content of 59.64% and 18.88% respectively.

The sum of the CaO and SiO₂ content gave 78.52% and loss on ignition of 3.0% which satisfy the standard limit of EN 197–1. Chemically, the OPC could be considered as good cement.

Also, the SiO₂ content of 18.37%, 16.53%, 15.07% and 19.05% and the corresponding loss on ignition of the clay pozzolana passed the requirements specified by the EN 197-1. The sum of SiO₂, Fe₂O₃ and Al₂O₃ content in the pozzolana exceeded the minimum value of 70% required by ASTM C 618. All the pozzolana cement samples had Cl and SO₃ contents lower than 0.1% and 4.5% respectively. The chemical (oxide) composition of the 10% pozzolana cement as given shows 59.18% CaO, 1.54% MgO and 18.37% SiO₂ content. The alumina (Al₂O₃) and iron oxide contents (Fe₂O₃) were 2.65% and 4.46% respectively. The CaO, SiO₂, Al₂O₃ and MgO content of all the pozzolana cements were within acceptable limits as prescribed by EN 196-2. The clay pozzolana and pozzolana cement samples could also be considered as chemically suitable.

4.2.1 X-ray diffraction (XRD)

Figure 4.2 shows the X-ray diffraction pattern of ordinary Portland cement (OPC) used for this study. The diffraction analysis shows the presence of four phases: Alite (C₃S, 3CaO.SiO₂), Belite (C₂S, 2CaO.SiO₂), Aluminate (C₃A, CaO.Al₂O₃) and Ferrite (C₄AF, 4CaO.Al₂O₃.Fe₂O₃). The diffraction peaks of C₃S, which is the most important phase, is more pronounced as compared to the other phases. Table 4.3 gives the mineralogical composition of the OPC with total calcium silicate content of 77.62%.



2θ

Figure 4.2: X-ray diffraction graph of ordinary Portland cement used for this study

Table 4.3: Mineralogical composition of OPC

Bogue potential composition, %			
C ₃ S	C ₂ S	C ₃ A	C ₄ AF
59.25	18.37	7.57	11.54

The X-ray diffraction of the clay pozzolana used for this study is also presented in Figure 4.3. The analysis shows the presence of kaolinite, quartz, calcite and goethite. The diffraction peaks relative to quartz was more pronounced between 20 and 30θ as compared to the other phases. From Figure 4.3, the clay pozzolana contains hydrated aluminosilicates needed to react with portlandite (Ca(OH)₂) released when Portland cement hydrates.

Table 4.4: Water demand and setting times of cement pastes with different pozzolana contents

Reference material (OPC)									
Water demand, %		Initial setting time, min				Final setting time, min			
28.5		155				245			
10% Pozzolana Cement									
Activator content, %	CaCl ₂			Na ₂ SO ₄			AlCl ₃		
	Water Demand, %	Setting times, mins		Water Demand, %	Setting times, mins		Water Demand, %	Setting times, mins	
		Initial	Final		Initial	Final		Initial	Final
0	32.8	162	272	32.8	162	272	32.8	162	272
1	32.8	162	265	32.8	155	243	32.8	162	265
2	32.8	150	245	32.8	140	240	32.8	159	264
3	32.8	131	230	32.8	122	220	32.8	158	255
4	32.8	122	212	32.8	115	200	32.8	150	240
20% Pozzolana Cement									
0	33.6	178	285	33.6	178	285	33.6	178	285
1	33.6	170	261	33.6	162	240	33.6	170	265
2	33.6	153	230	33.6	147	230	33.6	162	241
3	33.6	133	215	33.6	131	203	33.6	140	230
4	33.6	130	201	33.6	120	183	33.6	134	210
30% Pozzolana Cement									
0	35.6	184	310	35.6	184	310	35.6	184	310
1	35.6	180	288	35.6	178	255	35.6	179	280
2	35.6	160	261	35.6	150	224	35.6	177	262
3	35.6	130	225	35.6	130	200	35.6	140	235
4	35.6	128	210	35.6	125	182	35.6	130	220
40% Pozzolana Cement									
0	36.1	210	330	36.1	210	330	36.1	210	330
1	36.1	210	300	36.1	202	290	36.1	210	310
2	36.1	172	268	36.1	160	245	36.1	170	273
3	36.1	150	230	36.1	142	221	36.1	148	228
4	36.1	142	210	36.1	131	206	36.1	146	215

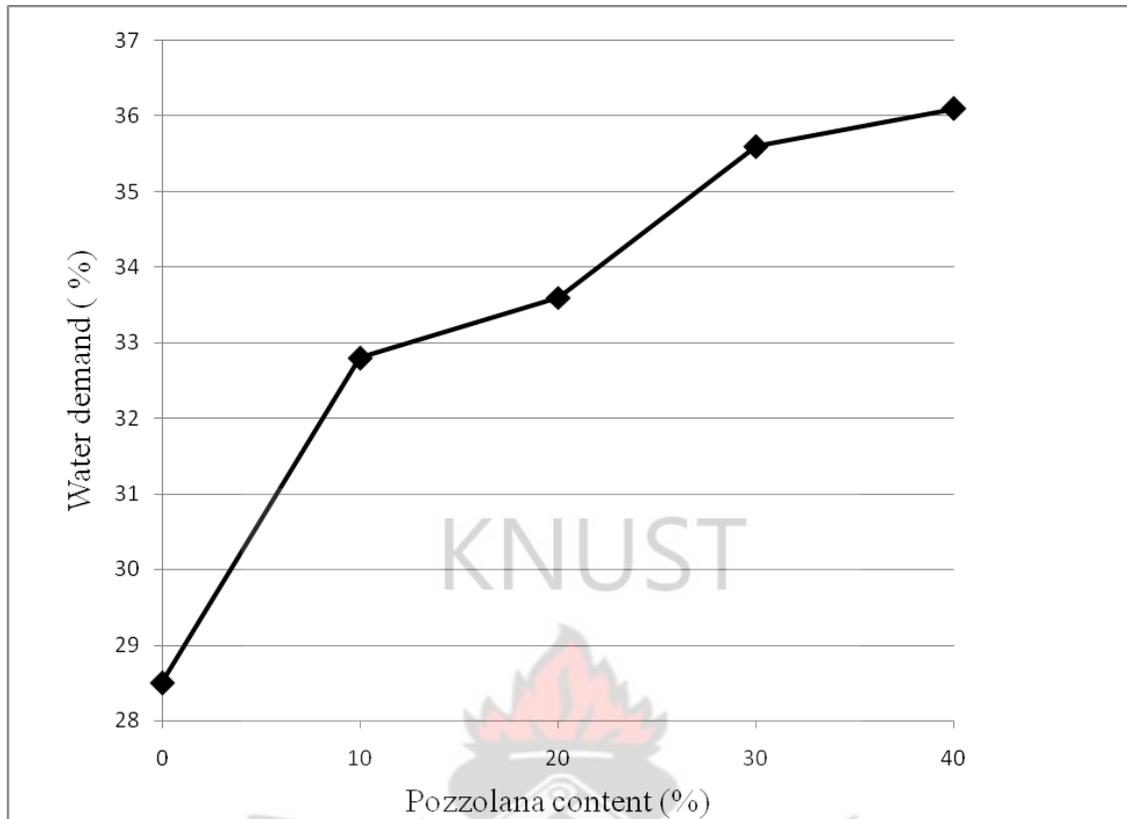


Figure 4.4: Water demand of cement pastes with different pozzolana content

It is clear that water demand to form a workable paste increased with increase in the pozzolana content. This progressive increase in water demand is due to the smaller particle size of the pozzolana which increases the surface area of the whole mix translating into higher water demand (Memon *et al.*, 2011). Therefore, as the pozzolana content increases, the surface area becomes greater thereby requiring greater volume of water to form a workable paste. Also, as the specific gravity increases with increasing pozzolana content, the equal volume of water required to form a workable paste increases. However, from Tables 4.4, the addition of CaCl_2 , Na_2SO_4 , and AlCl_3 had no effect on the water demand.

4.3.2 Setting times

4.3.2.1 10% pozzolana cement

Figure 4.5 shows the initial and final setting times of cement paste with 10% pozzolana content containing CaCl_2 , Na_2SO_4 and AlCl_3 at different percentages. From Figure 4.5, the initial setting time of the pozzolana cement paste without any chemical admixture (0%) recorded initial and final setting times of 162 and 272 minutes which were about 12 and 27 minutes higher than the control (OPC). The addition of either 1% CaCl_2 or 1% AlCl_3 did not affect the initial setting time but decreased the final setting time by 2.6% respectively. There was a progressive decrease in both the initial and final setting time as the activator dosage increased from 2% to 4% for CaCl_2 and AlCl_3 . With the addition of 2% CaCl_2 , the initial setting time of the paste was about 3.2% faster than the control whereas the final setting recorded the same time as the control.

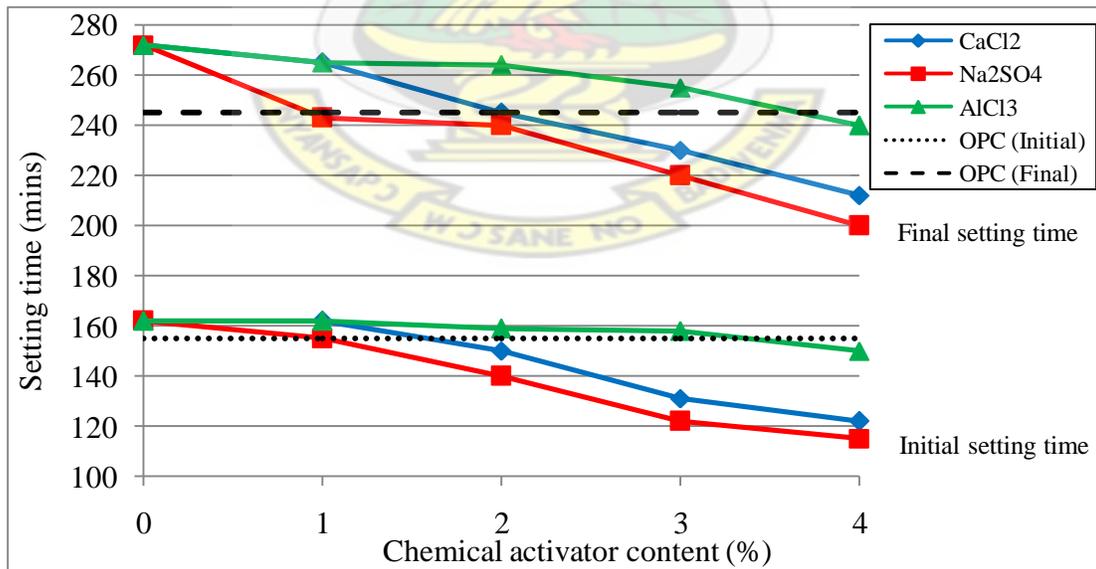


Figure 4.5: Setting times of cement pastes with 10% pozzolana content containing CaCl_2 , Na_2SO_4 and AlCl_3 at different percentages.

The activation of the 10% pozzolana cement paste with Na_2SO_4 decreased the initial and final setting time at all dosage levels. The addition of 1% Na_2SO_4 decreased the initial setting to the time of the control (155 mins) whereas the final setting of the paste was 0.8% faster than the control. The addition of 2%, 3% or 4% Na_2SO_4 caused the paste to record initial setting times about 9.7%, 21.3% or 25.8% faster than the control whereas the final setting times were about 2%, 10.2% or 14.4% faster.

Comparatively, Na_2SO_4 had the greatest effect on the setting of cement paste containing 10% pozzolana, producing a significant set accelerator at all percentages. CaCl_2 also caused noticeable reductions in the initial and final setting times although not as effective as Na_2SO_4 but however performed better than AlCl_3 .

The increase in setting time as a result of the incorporation of pozzolana is because the reaction between the pozzolana constituents and $\text{Ca}(\text{OH})_2$ is a very sluggish one (Guo, 1986). The addition of the chemical activators increases the dissolution rate of $\text{Ca}(\text{OH})_2$ thereby increasing the rate of pozzolanic reaction (Shi and Day, 2000), decreasing the rate of setting of the paste.

4.3.2.2 20% pozzolana cement

Figure 4.6 shows the effect of CaCl_2 , Na_2SO_4 and AlCl_3 at different percentages on the initial and final setting time of 20% pozzolana cement paste. It is observed that, the paste, without activator, recorded initial and final setting times of 178 and 285 minutes, which were about 14.8% and 16.3% higher than the control paste.

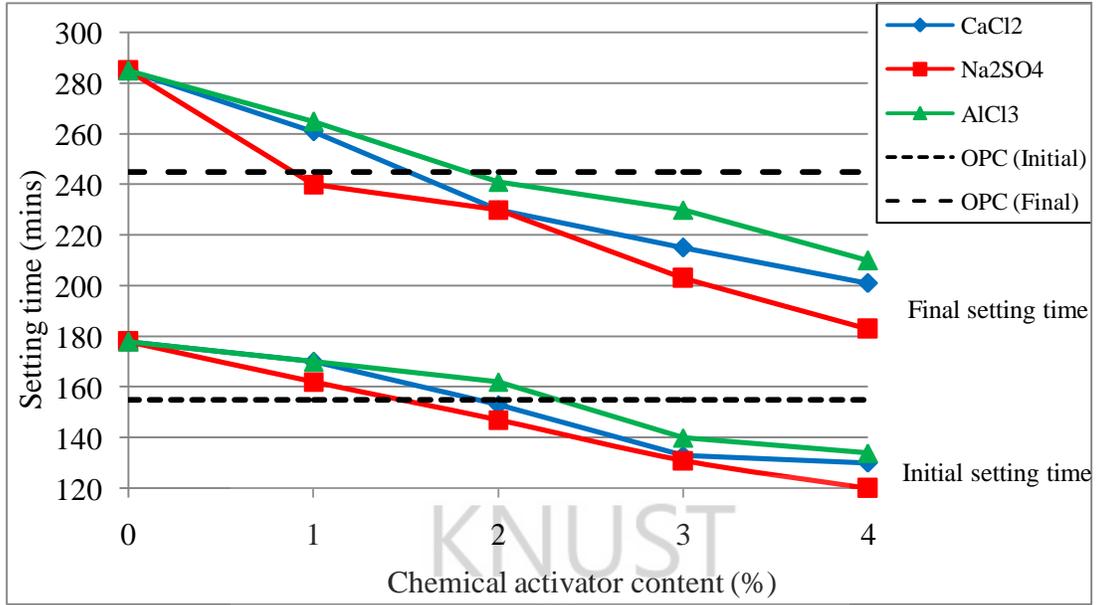


Figure 4.6: Setting times of cement paste with 20% pozzolana content containing CaCl₂, Na₂SO₄ and AlCl₃ at different percentages.

The addition of 1% of CaCl₂, Na₂SO₄ and AlCl₃ caused reductions in the initial setting times but the reductions were not enough to make up for the 20% pozzolana inclusion. There were further reductions in initial setting times as the chemical dosage was increased from 1% to 4%. The addition of 2% CaCl₂ reduced the initial setting time of the paste by 1.1% compared to the control whereas 2% Na₂SO₄ set about 8.4% faster than the control. The activation of the paste with 2% AlCl₃ on the other hand caused a reduction in the initial time of setting comparable to the paste without the activator but could not reduce it up to the initial setting time of the control until the dosage was increased to 3%.

Similarly, as the dosage levels for all the activators increased, the final setting times of the paste decreased. The activation of the paste with 1% CaCl₂ or 1% AlCl₃ caused 8.4% and 7.0% reductions respectively in the final setting times. However, these reductions were not

enough to discount the pozzolanic effect. Setting times lower than the control paste was achieved when the dosage was increased to 2%. On the other hand, the paste containing 1% Na_2SO_4 recorded final setting time less than the control paste and progressively decreased as the dosage increased.

4.3.2.3 30% pozzolana cement

As presented in Figure 4.7, with the incorporation of 30% pozzolana in the cement paste, the initial and final setting time recorded were 184 and 310 minutes respectively which were about 29 and 65 minutes higher than the control. The activation of the pozzolana cement paste with 1% CaCl_2 , Na_2SO_4 or AlCl_3 caused 2.2%, 3.3%, and 2.7% reductions respectively in the initial setting time and 7.1%, 3.3% and 2.7% respectively in the final setting time, but always higher than the control. There was however a progressive decrease in the setting times as the dosage increased from 1% to 4%. 2% Na_2SO_4 had a profound effect giving setting times lower than the control. None of the activators was able to record initial and final setting times equal or lower than the control.

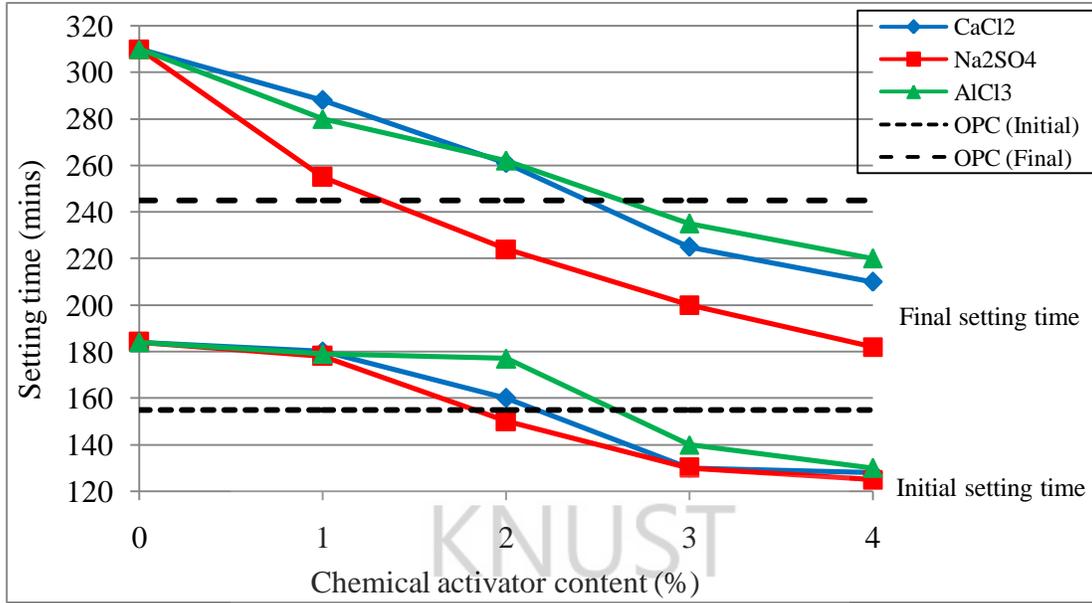


Figure 4.7: Setting times of cement paste with 30% pozzolana content containing CaCl₂, Na₂SO₄ and AlCl₃ at different percentages.

However, the addition of 3% of CaCl₂, Na₂SO₄ or AlCl₃ caused the paste to have setting times (both initial and final) lower than the control paste, discounting the effect of the 30% pozzolana inclusion. The final setting times obtained percentage reductions of 8.2%, 18% and 4% respectively compared to the control.

4.3.2.4 40% pozzolana cement

Figure 4.8 shows the effect of CaCl₂, Na₂SO₄ and AlCl₃ at different percentages on the initial and final setting time of 40% pozzolana cement paste. It is observed that the replacement of OPC with 40% clay pozzolana caused the paste to record high initial and final setting times of 210 and 330 minutes respectively. The addition of 1% CaCl₂ or AlCl₃ did not affect initial setting time but decreased slightly final setting time by 14.2% and 9.5% respectively.

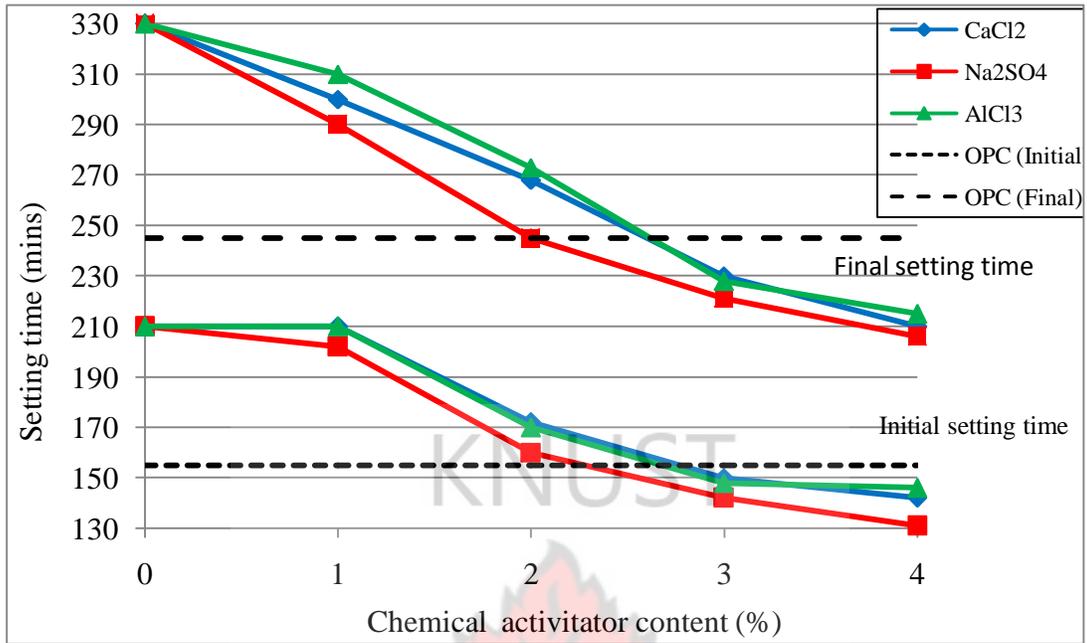


Figure 4.8: Setting times of cement paste with 40% pozzolana content containing CaCl₂, Na₂SO₄ and AlCl₃ at different percentages.

On the other hand, the activation of the paste with 1% Na₂SO₄ recorded reductions in both initial and final setting times. Beyond 1%, there was a progressive decrease in both initial and final setting times of all the activated pastes. The addition of the paste with 2% CaCl₂, Na₂SO₄ or AlCl₃ decreased the final time of setting by 18.8%, 25.8% and 17.3% respectively. It is observed that the paste activated with 2% Na₂SO₄ recorded final setting time equal to that of the control. With the activation of the paste with 3% CaCl₂, Na₂SO₄ or AlCl₃, the paste recorded initial and final setting times lower than that of the control. It is also observed that the paste activated with 4% Na₂SO₄ obtained final setting time lower than the initial setting time of the unactivated pozzolana cement paste.

4.4 Compressive strength

The minimum standard requirements of compressive strengths for cement mortar cubes by the European Standards, Ghana Standards and the American Society for Testing Materials standard are presented in Table 4.5. The results for the compressive strength determinations are given in Table 4.6. The data are also represented graphically in Figures 4.9 – 4.20.

Table 4.5: Standard requirement for compressive strengths of cements

Standard	2 days	7 days	28 days	Class
EN	10	16	32.5	42.5
ASTM	–	–	24.1	–
GS 22	10	16	32.5	42.5

4.4.1 10% Pozzolana cement

Figures 4.9 – 4.11 show the effect of CaCl_2 , Na_2SO_4 and AlCl_3 on compressive strength development of 10% pozzolana cement mortar cube at 2, 7 and 28 days. It is observed that, with the application of 1% of all the three activators, the strength at 2 days increased by 8.0%, 12.2%, and 6.0% respectively. Also, the strengths increased by 1.3%, 11.2%, and 1.7% at 7 days; and by 0.7%, 1.1%, and 1.1% at 28 days. The specimen containing 2 – 4% Na_2SO_4 outperformed the reference sample (control) by 2.2%, 14.4% and 19.1% respectively at 2 days and 1.6%, 8.4% and 13.9% respectively at 7 days. Similarly, the cube containing 3% CaCl_2 outperformed the control by 1.3% and 11.4% respectively at 2 days and 6.2% and 13.4% respectively at 7 days. At early ages, the addition of 1% CaCl_2 , Na_2SO_4 and AlCl_3 could not compensate for the 10% OPC loss. The 2-day compressive

strengths of the AlCl_3 -activated samples, even though slowly approached the control as the dosage increased, could not exceed it, until the dosage was increased to 4%. From Figures 4.9 – 4.10, comparing the chemical activators, it is seen that Na_2SO_4 was the most effective in the early strength development, achieving the same strength as the control at 2% content whilst CaCl_2 achieved same or higher at 3%.

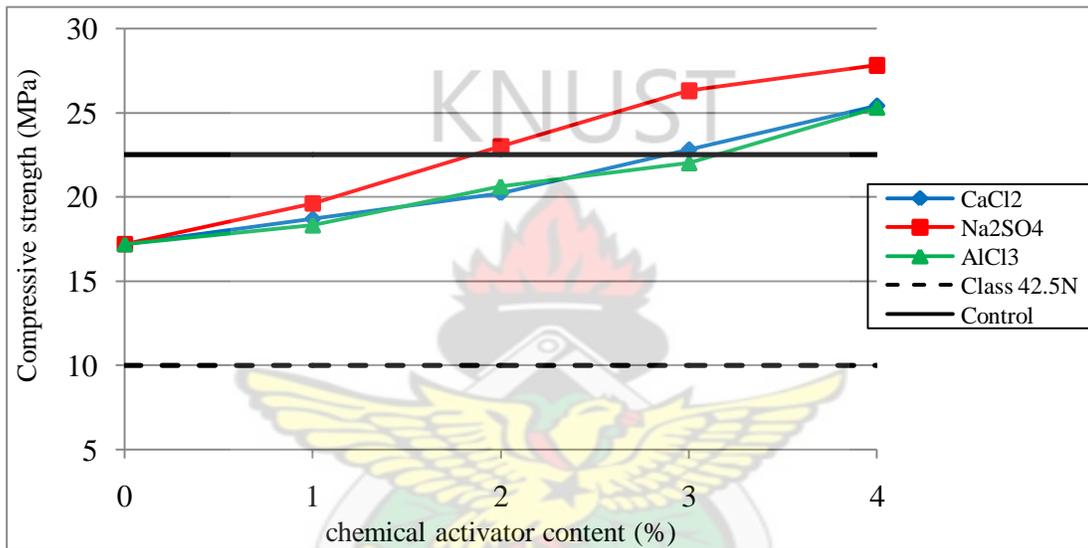


Figure 4.9: 2-day compressive strength of 10% pozzolana cement with chemical activators at different percentages.

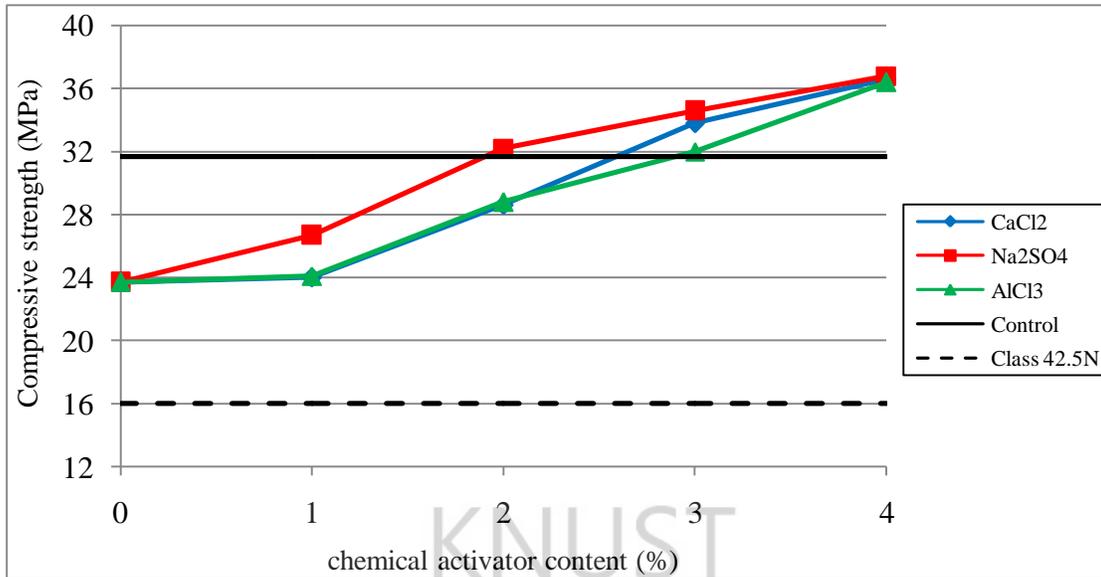


Figure 4.10: 7-day compressive strength of 10% pozzolana cement with chemical activators at different percentages.

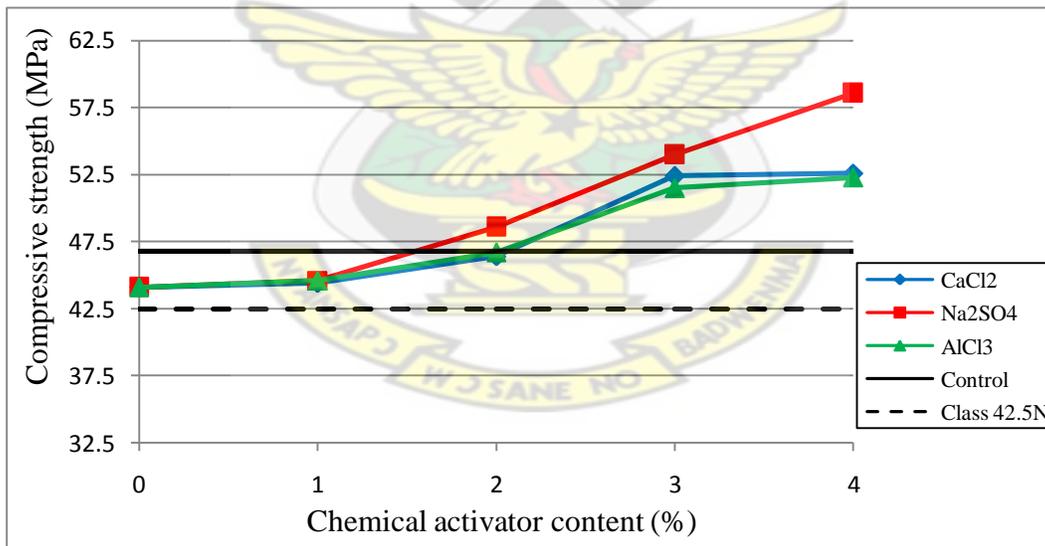


Figure 4.11: 28-day compressive strength of 10% pozzolana cement with chemical activators at different percentages.

At 28 days, 2% Na_2SO_4 exceeded the control strength by 3.8% whereas CaCl_2 and AlCl_3 trailed the strength of the control by 0.9% and 0.2% respectively. Beyond 2%, all the activators recorded strength gains greater than the control paste. From Figure 4.11, it is observed that AlCl_3 performed better at 28 days than at the early ages with 3% and 4% exceeding the strength of the control. CaCl_2 and Na_2SO_4 on the other hand performed better in both early and ultimate strength development.

However, all the mortar samples (with or without activator) exceeded the minimum strengths of 10MPa, 16MPa and 32.5MPa (2, 7 and 28 days respectively) required by EN 197-1. The higher early and ultimate strength development is because the presence of CaCl_2 , Na_2SO_4 or AlCl_3 in the pastes accelerated the early pozzolanic reaction and effectively, the consumption of $\text{Ca}(\text{OH})_2$ in the activated pastes. As the concentration of the activator increased, the $\text{Ca}(\text{OH})_2$ in the pastes declined more quickly (Shi and Day, 2000). However, the $\text{Ca}(\text{OH})_2$ in the control sample was consumed more quickly than that in the AlCl_3 -activated sample during the initial stages.

4.4.2 20% Pozzolana cement

The compressive strength development of 20% pozzolana cement paste at 2, 7, and 28 days have been graphically presented in Figures 4.12 – 4.14. It is observed that even though the strength of the mortar paste appreciated as the dosage of all activators increased, only the specimen containing 2% - 4% Na_2SO_4 and 3% - 4% CaCl_2 exceeded the control value at 2 and 7 days. At 2 days, the compressive strength of the specimen containing 2% Na_2SO_4 equalled the control but was about 5.6% higher than CaCl_2 and 26.4% higher than AlCl_3 . It

is observed from Figures 4.12 and 4.13 that the 2 and 7 days strength of the mortar samples containing 20% pozzolana was improved by 25.3% and 29.2% respectively by the addition of a minimum dosage of 2% Na₂SO₄. The strength however increased by 27.0% and 29.7% respectively with the addition of 3% CaCl₂.

Table 4.6: Compressive strength results of cement paste with different pozzolana content

Reference material (Control)									
<u>Compressive strength, Mpa</u>									
2 days			7 days			28 days			
22.5			31.7			46.8			
10% Pozzolana Cement									
Activator	CaCl ₂			Na ₂ SO ₄			AlCl ₃		
	<u>Compressive strength,</u>			<u>Compressive strength,</u>			<u>Compressive strength,</u>		
Content,	<u>MPa</u>			<u>MPa</u>			<u>MPa</u>		
	2 days	7 days	28 days	2 days	7 days	28 days	2 days	7 days	28 days
0	17.2	23.7	44.1	17.2	23.7	44.1	17.2	23.7	44.1
1	18.7	24.0	44.4	19.6	26.7	44.6	18.3	24.1	44.6
2	20.2	28.6	46.4	23	32.2	48.6	20.6	28.8	46.7
3	22.8	33.8	52.4	26.3	34.6	54.0	22.0	32.0	51.5
4	25.4	36.6	52.6	27.8	36.8	58.6	25.3	36.4	52.3
20% Pozzolana Cement									
0	16.8	22.5	40.0	16.8	22.5	40	16.8	22.5	40.0
1	17.2	23.2	40.7	18.1	26.8	41.2	17.3	24.3	40.3
2	21.3	28.6	43.4	22.5	31.8	47.0	17.8	24.8	40.5
3	23.0	32.0	46.9	24.9	32.8	48.6	17.8	25.4	41.1
4	25.0	32.8	48.6	25.8	33.6	54.2	19.0	30.0	48.6
30% Pozzolana Cement									
0	16.1	20.0	39.0	16.1	20.0	39.0	16.1	20.0	39.0
1	16.4	20.0	39.8	17.2	21.8	41.6	16.5	20.3	41.0
2	18.6	23.5	41.2	22.5	28.2	43.1	17.5	22.6	41.4
3	22.5	32.1	42.4	25.8	33.3	45.2	19.0	23.4	41.8
4	23.8	32.6	46.8	27.7	34.2	48.8	22.0	32.1	46.6
40% Pozzolana Cement									
0	13.3	16.2	30.5	13.3	16.2	30.5	13.3	16.2	30.5
1	14.6	17.4	31.6	16.0	18.0	32.6	14.3	17.1	31.8
2	17.1	21.5	33.4	18.0	24.3	35.4	16.3	20.7	33.6
3	18.2	25.8	36.5	21.3	27.6	39.4	19.8	24.6	37.1
4	21.3	30.0	40.0	25.8	33.2	41.8	20.6	29.5	39.8

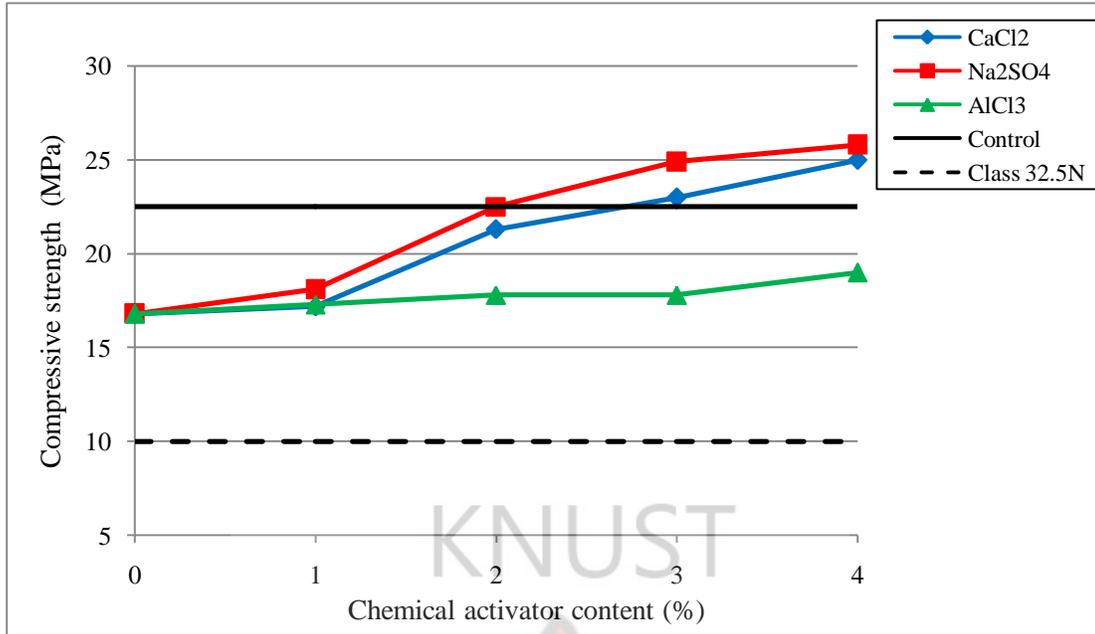


Figure 4.12: 2-day compressive strength of 20% pozzolana cement with chemical activators at different percentages.

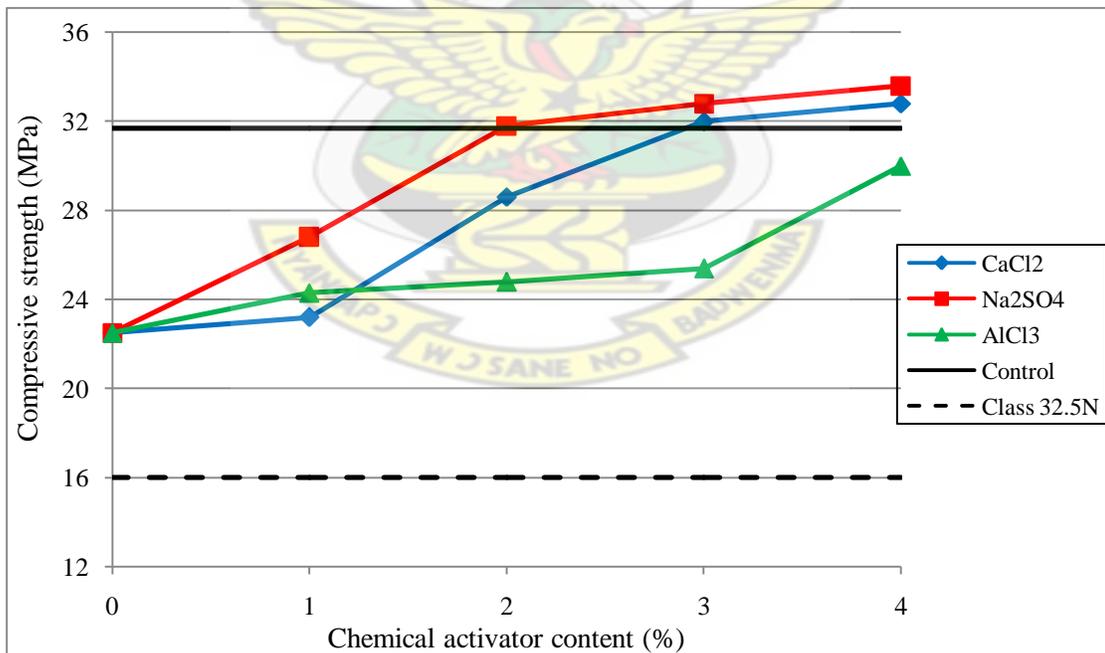


Figure 4.13: 7-day compressive strength of 20% pozzolana cement with chemical activators at different percentages.

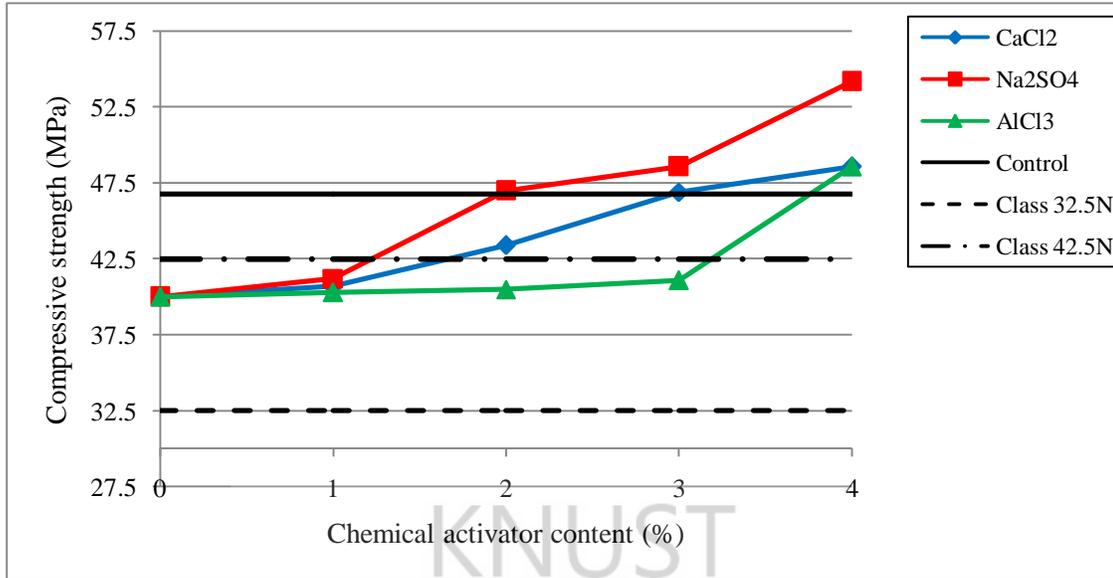


Figure 4.14: 28-day compressive strength of 20% pozzolana cement with chemical activators at different percentages.

From Figure 4.14, the 28-day strength increased with increase in activator dosage, thus outperforming the sample without any chemical activator (0%) by at least 14.5%. The compressive strength of the control was exceeded by 0.4%, 0.2% and 3.7% when 2% Na₂SO₄, 3% CaCl₂ or 4% AlCl₃ respectively was added to the mortar samples and also satisfied class 42.5N (EN 197-1). However, all the mortar samples (with or without activator) exceeded the minimum strengths of 10MPa, 16MPa and 32.5MPa (2, 7 and 28 days respectively) required by EN 197-1 (EN 197, 2000) by class 32.5N cement.

4.4.3 30% Pozzolana cement

Figures 4.15 – 4.17 show the effect of the chemicals on compressive strength development of 30% pozzolana cement mortar paste at 2, 7 and 28 days. Similarly, the compressive strength at all ages increased as the activator concentration increased from 1% to 4%. At 2

days, the addition of 2% Na_2SO_4 or 3% CaCl_2 equalled the control value whereas 4% AlCl_3 approached the control value closely but trailed it by 2.3%. It is observed that at 7 days, a higher dosage (3%) of Na_2SO_4 was required to increase the strength by 4.8% above the control value. The specimen containing 3% Na_2SO_4 outperformed the control specimen by 5.0% whereas the specimen containing 3% CaCl_2 exceeded it by 1.3%. Beyond 3% dosage, addition of all the chemical activators to the mortar samples recorded strengths greater than the control by 2.8%, 7.3% and 1.2% respectively at 7 days.

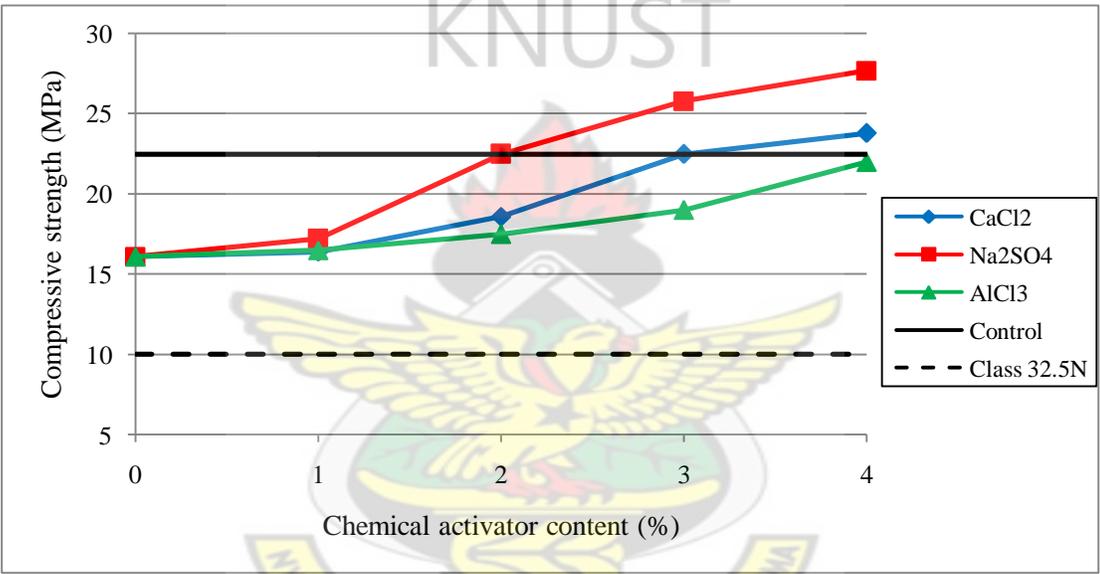


Figure 4.15: 2-day compressive strength of 30% pozzolana cement with chemical activators at different percentages.

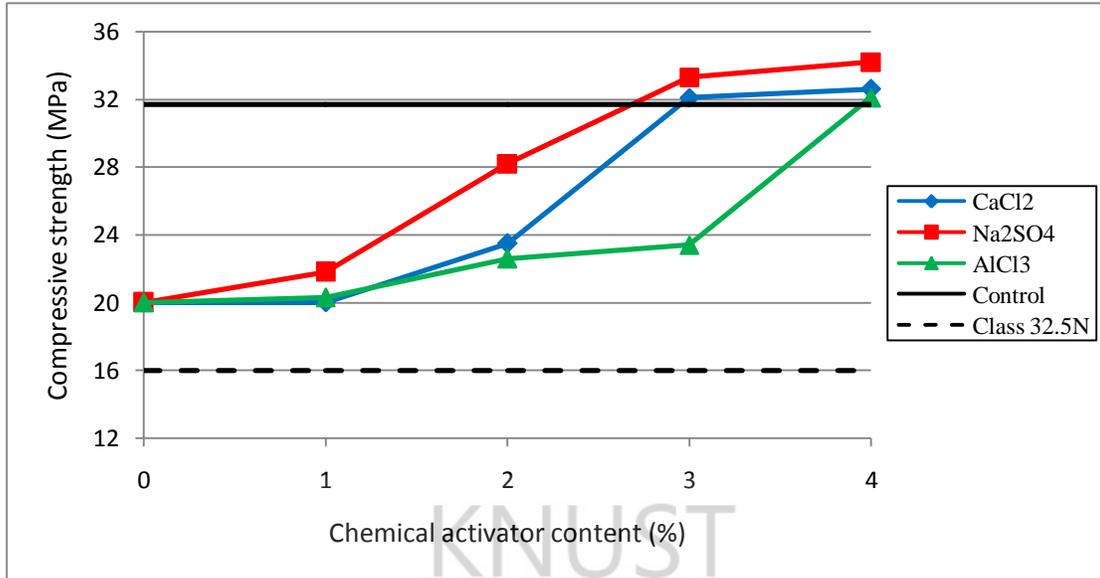


Figure 4.16: 7-day compressive strength of 30% pozzolana cement with chemical activators at different percentages.

As the age increased to 28 days, a higher dosage was required to increase the strength up to the control value. The addition of 4% CaCl₂ equalled the control value whereas 4% Na₂SO₄ exceeded it by 4.3%. The addition of 1% – 4% AlCl₃ however could not compensate for the 30% cement replacement. With the addition of 2% CaCl₂, 1% Na₂SO₄ or 3% AlCl₃, the 30% pozzolana cement mortar recorded strengths of 41.2 MPa, 41.6 MPa, and 41.8 MPa respectively, making it behave as Class 42.5 cement. It is also observed that all the samples at different concentration exhibited an initial and a later strength gain. This is because the addition of the chemical activators increases the alkalinity of the solution and the dissolution of the pozzolana at initial stages, which accelerates the pozzolanic reaction between lime and pozzolana (Shi and Day, 1995).

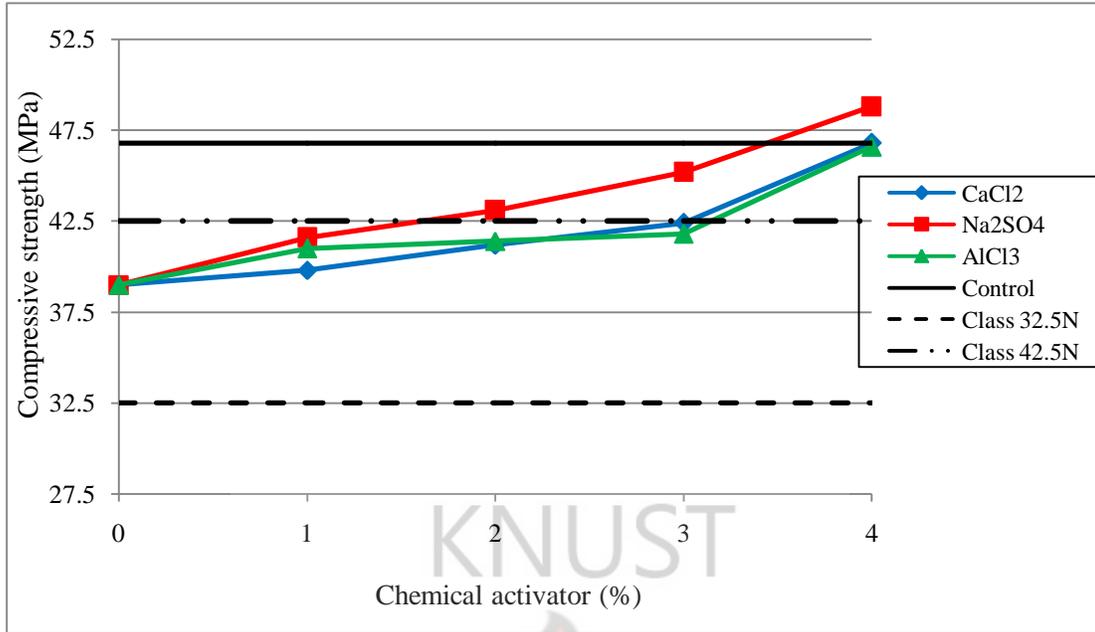


Figure 4.17: 28-day compressive strength of 30% pozzolana cement with chemical activators at different percentages.

4.4.4 40% Pozzolana cement

The compressive strength development of 40% pozzolana cement paste at 2, 7, and 28 days have been graphically presented in Figures 4.18 – 4.20. It can be seen that even though there was significant increase in compressive strength at both early and later ages, the high 40% replacement with clay pozzolana could not be compensated by the addition of CaCl₂ or AlCl₃, even at 4%. This could be attributed to the dilution effect. Also, as the pozzolana content in the cement increased, the pozzolanic reactivity decreased thereby decreasing the rate of Ca(OH)₂ consumption in the paste. However, the activation of the 40% pozzolana cement with 4% Na₂SO₄ improved significantly the early strength, exceeding the control value by 14.7% at 2 days and 4.7% at 7 days.

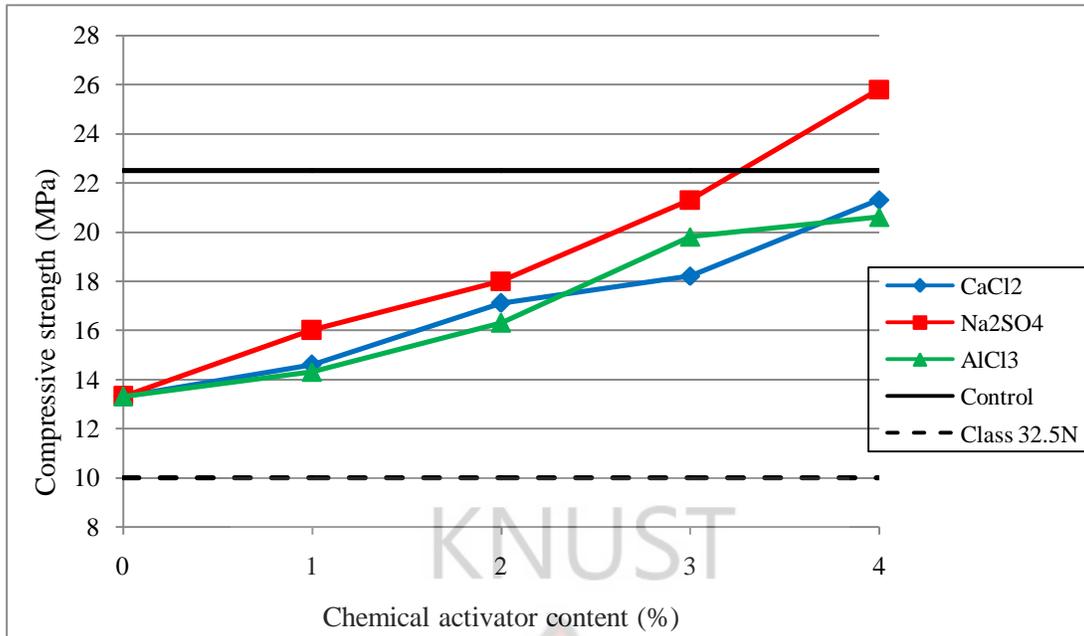


Figure 4.18: 2-day compressive strength of 40% pozzolana cement with chemical activators at different percentages.

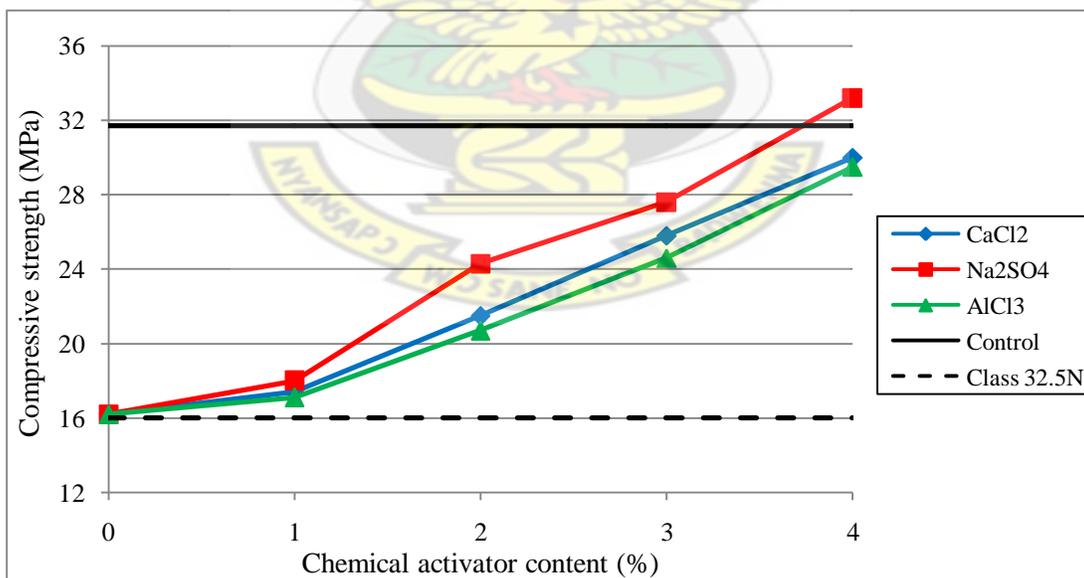


Figure 4.19: 7-day compressive strength of 40% pozzolana cement with chemical activators at different percentages.

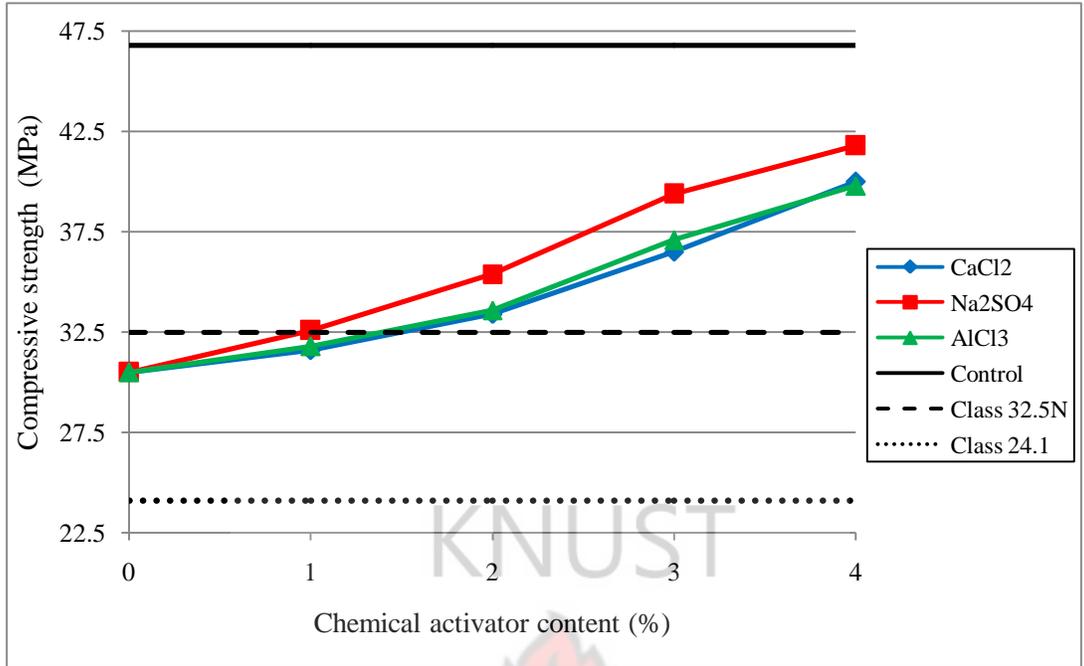


Figure 4.20: 28-day compressive strength of 40% pozzolana cement with chemical activators at different percentages.

At 28 days, the paste without any chemical activator recorded strength lower than the minimum strength of 32.5MPa required by the EN 197-1 Standard but higher than the 24.1MPa required by ASTM C595 Standard. However, the presence of CaCl₂, Na₂SO₄ or AlCl₃ considerably increased the strengths above the EN 197-1 Standard but below the control value.

4.5 Water permeability

Results of water permeability test are presented in Table 4.7 and graphically in Figure 4.21. Test data showed that water absorption decreased as Na₂SO₄ concentration in the paste increased. From Table 4.7, OPC recorded co-efficient of water absorption (K_a) of 5.40×10^{-04} m/s which was decreased by 9.4% when OPC was replaced with 30%

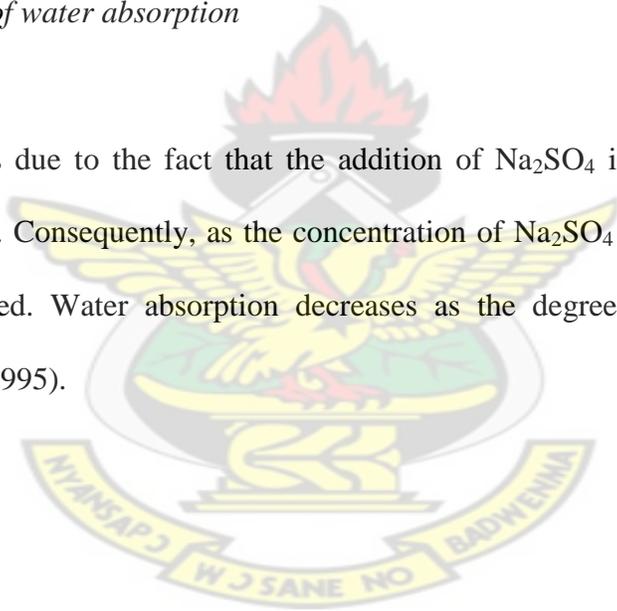
pozzolana. A further reduction of about 15% was recorded when 1% Na₂SO₄ was added to the paste. *K_a* progressively decreased as the concentration of Na₂SO₄ increased from 1% – 4%. At 4%, the total reduction of the co-efficient of water absorption was about 32.7%.

Table 4.7: Water permeability test results of 30% pozzolana cement containing Na₂SO₄

Sample	OPC	Na ₂ SO ₄ content (%)				
		0%	1%	2%	3%	4%
<i>K_a</i>	5.40×10 ⁻⁰⁴	4.89×10 ⁻⁰⁴	4.16×10 ⁻⁰⁴	3.94×10 ⁻⁰⁴	3.71×10 ⁻⁰⁴	3.29×10 ⁻⁰⁴

K_a – co-efficient of water absorption

The decrease was due to the fact that the addition of Na₂SO₄ increased the rate of the hydration process. Consequently, as the concentration of Na₂SO₄ increased, the degree of hydration increased. Water absorption decreases as the degree of hydration increases (Ramachandran, 1995).



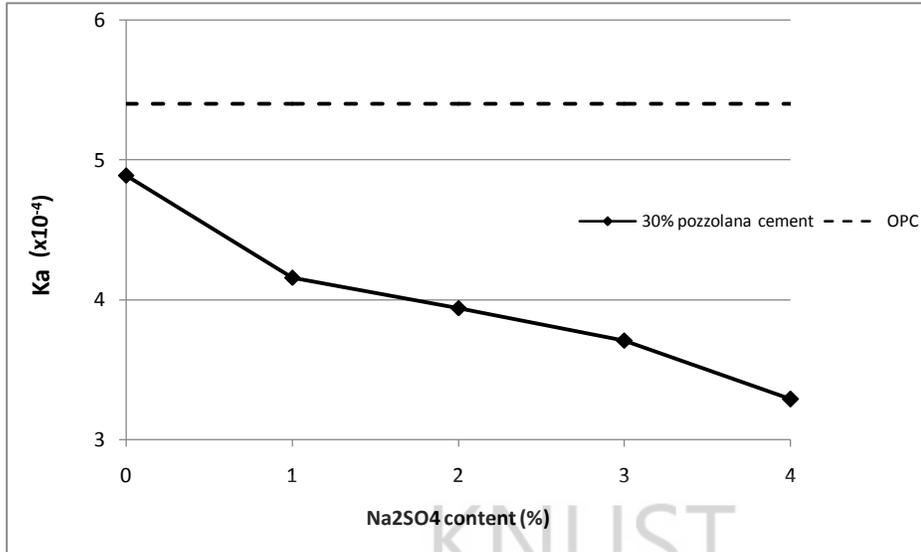


Figure 4.21: Water absorption test results of 30% pozzolana cement containing Na₂SO₄.

4.6 Significant results from study

4.6.1 Setting time

The incorporation of 30% clay pozzolana in cement paste increased the initial and final setting times of the paste by 18.7% and 42% respectively. However, the addition of the three chemical activators caused a progressive decrease in both the initial and final setting times as the activator dosage increased from 1% – 4%. The activation of the paste with 2% Na₂SO₄, 3% CaCl₂ or 3% AlCl₃ caused the paste to have initial and final setting times lower than the reference material, discounting the effect of the pozzolana inclusion. From the results obtained in this study, 2% Na₂SO₄, 3% CaCl₂ or 4% AlCl₃ is considered as the optimum dosage required to accelerate the initial and final setting times of 30% pozzolana

cement to equalize or even set faster than the reference material. Figure 4.22 presents the optimum percentage required to accelerate the setting time of 30% pozzolana cement.

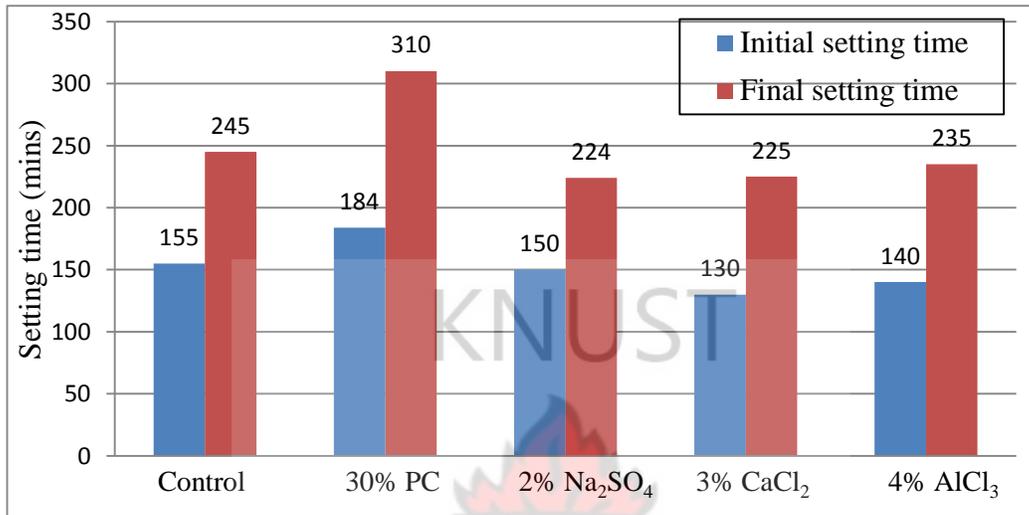


Figure 4.22: Optimum percentage required to improve the setting time of pozzolana cement.

4.6.2 Compressive strength

The dilution effect of replacing 30% of OPC with clay pozzolana caused the compressive strength of the reference material to reduce by 28.4% at 2 days, 37% at 7 days and 16.7% at 28 days. However, the strength at 2, 7, and 28 days increased as the activator concentration increased from 1% – 4%. From the study, 2% Na₂SO₄, 3% CaCl₂ or 4% AlCl₃ is the optimum dosage required to increase the 2-day strength to equal that of the reference material whereas 3% Na₂SO₄, 3% CaCl₂ or 4% AlCl₃ is the optimum dosage at 7 days. At 28 days, the activation of the mortar with 1% Na₂SO₄, 2% CaCl₂ or 3% AlCl₃ increased the compressive strength, making it record strengths close to Class 42.5 cement.

Figure 4.23 represents the optimum percentage required to improve early strength of pozzolana cement.

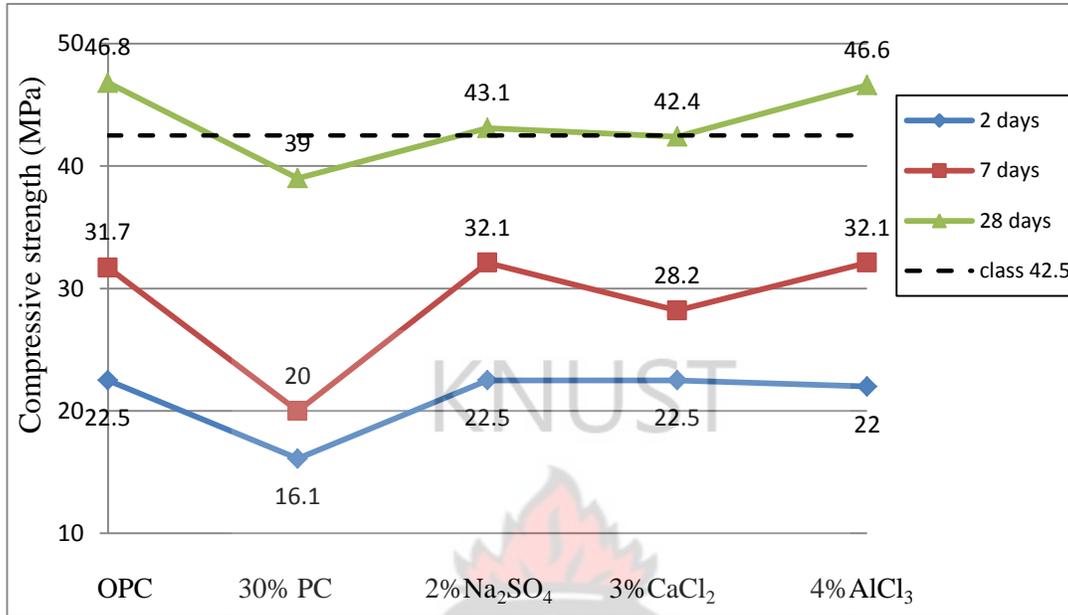


Figure 4.23: Optimum percentage required to improve the early strength of pozzolana cement.

4.7 Economic analysis of chemically activated pozzolana cements

As presented in Table 4.8, the incorporation of 30% pozzolana in OPC causes about 17.7% reduction in cost. However, the activation of 30% pozzolana cement with 2% Na₂SO₄, 3% CaCl₂ or 4% AlCl₃ slightly increases the unit cost of pozzolana cement but still about 16.7%, 16.2% or 13.1% less expensive than OPC.

The results confirm the research carried out by Shi and Day (2001) that chemical activation is an efficient and less expensive method of activating the potential reactivity of pozzolanas.

Table 4.8: Cost of raw materials

No.	Material	Cost (GHC/ton)
1	Pozzolana	180
2	Portland cement	440
3	Na ₂ SO ₄	220
4	CaCl ₂	220
5	AlCl ₃	506
6	70% OPC + 30% pozzolana	362
7	[70% OPC + 30% pozzolana] + 2% Na ₂ SO ₄	366.4
8	[70% OPC + 30% pozzolana] + 2% CaCl ₂	366.4
9	[70% OPC + 30% pozzolana] + 3% CaCl ₂	368.6
10	[70% OPC + 30% pozzolana] + 3% AlCl ₃	377.2
11	[70% OPC + 30% pozzolana] + 4% AlCl ₃	382.2



CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study has investigated the early strength development and setting time acceleration of cement samples containing 10%, 20%, 30% and 40% clay pozzolana content in the presence of 1%–4% Na_2SO_4 , CaCl_2 and AlCl_3 . The following conclusions are drawn based on the experimental results:

- The OPC recorded a specific gravity of 3.18 whereas clay pozzolana obtained the least value of 2.67. However, the specific gravity and Blaine indices of the pozzolana cement decreased as the pozzolana content in the mix increased. This indicates that the surface area of the mix also increased with increasing pozzolana content;
- The particle size analysis performed showed that clay pozzolana had particles ranging between 0.000139 – 0.3mm whereas that of sand ranged between 0.14 – 2.4mm. This confirms that the sand and pozzolana were uniformly graded;
- The clay pozzolana samples used for this work contained adequate amounts of reactive silica and alumina, obtaining silica content above the minimum limit of 25% as required by EN 197-1. The sum of the SiO_2 , Al_2O_3 and Fe_2O_3 content of all the samples was above the ASTM C 618 minimum standard of 70%;
- The sum of CaO and SiO_2 of the OPC studied was greater than 50% and recorded an LOI below 3.5% as specified by EN 197-1. The OPC could therefore be said to be chemically suitable;

- The XRD analysis of the OPC showed the presence of enough Alite (C_3S , $3CaO.SiO_2$) and the clay pozzolana contained enough aluminosilicate making them chemically suitable;
- Water demand or normal consistency progressively increased with increasing pozzolana content. OPC recorded the least (28.5%) whereas 40% pozzolana cement obtained the highest (36.1%). The addition of $CaCl_2$, Na_2SO_4 , and $AlCl_3$ had no effect on the water demand. The water demand of the mixes remained unchanged at all dosage levels;
- The initial and final setting times of the pozzolana cement increased significantly because of the incorporation of large volumes of pozzolana;
- Addition of $CaCl_2$, Na_2SO_4 , and $AlCl_3$ accelerated both initial and final setting times of pozzolana cement pastes. Generally, as the dosage level of the chemical activators in the mix increased from 1 – 4%, both initial and final setting times significantly reduced;
- As pozzolana content in the mix increased, setting times increased greatly, therefore higher dosage levels of the chemical activators were required to reduce the setting times to equal that of the control paste or even set faster than the control;
- For the studied pozzolana cements, sodium sulphate (Na_2SO_4) is the most effective chemical activator for accelerating setting times compared to $CaCl_2$ and $AlCl_3$, with $CaCl_2$ performing better than $AlCl_3$. The addition of 2% Na_2SO_4 was able to cause significant reductions in initial and final setting times of mortar paste containing 30% pozzolana, setting faster than the control paste;

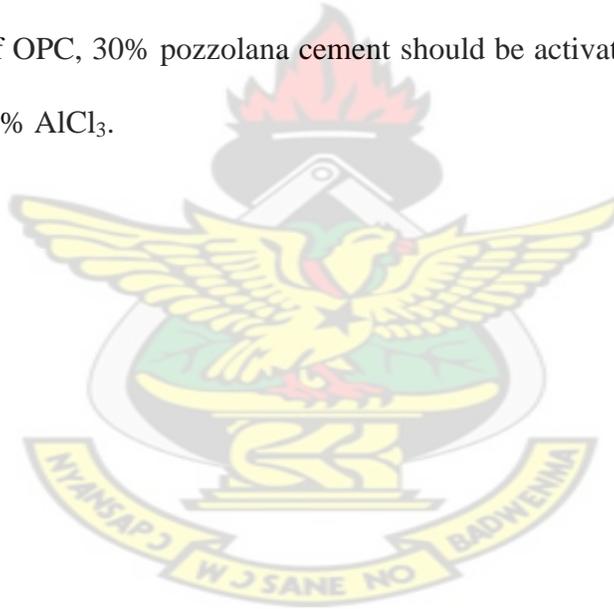
- Based on the setting time development, the optimum dosage is 2% Na_2SO_4 , 3% CaCl_2 or 3% AlCl_3 ;
- The setting times and standard consistencies of the pozzolana cement samples were all within acceptable standards (EN 197-1);
- Compressive strengths (2, 7 and 28 days) of pozzolana cement mortar cubes decreased with increasing pozzolana content. The incorporation of OPC with 40% pozzolana recorded about 34.8% reduction in the 28-day compressive strength;
- The addition of CaCl_2 , Na_2SO_4 , or AlCl_3 significantly improved both early and later strengths of the pozzolana cement studied;
- As pozzolana content increased in the mix, higher dosages of the chemical activators were required to increase both early and later strengths;
- Na_2SO_4 is the most effective chemical activator in improving early and later strengths of pozzolana cement mortars as compared to CaCl_2 and AlCl_3 . The addition of 2% Na_2SO_4 improved the 2-day strength of 20% and 30% pozzolana cement by 25.3% and 28.4% respectively;
- The early strength of the paste containing 20% pozzolana is improved greatly by the addition of a minimum dosage of 2% Na_2SO_4 or 3% CaCl_2 ;
- At 28 days, the compressive strength of the control was exceeded when 2% Na_2SO_4 , 3% CaCl_2 or 4% AlCl_3 was added to the paste;
- At 2 days, the 30% pozzolana cement paste activated with 2% Na_2SO_4 or 3% CaCl_2 recorded strengths equal to the control whereas 4% AlCl_3 approached the control value closely but trailed it by 2.3%. At 28 days, the addition of 4% CaCl_2

reached the control value whereas 4% Na_2SO_4 exceeded it by 4.3%. The addition of 1% – 4% AlCl_3 however could not compensate for the 30% cement replacement;

- The activation of 40% pozzolana cement paste with up to 4% CaCl_2 or AlCl_3 , even though increased significantly both early and later strengths, could not compensate for the heavy 40% pozzolana inclusion. However, the activation of the 40% pozzolana cement with 4% Na_2SO_4 improved significantly the early strength, exceeding the control value by 14.7% at 2 days and 4.7% at 7 days;
- At 28 days, the unactivated 40% pozzolana cement paste recorded strength lower than the minimum strength required by the EN 197-1 Standard but higher than ASTM C595 standard. However, the presence of CaCl_2 , Na_2SO_4 or AlCl_3 considerably increased the strengths above the EN 197-1 standard but below the control value;
- Water permeability in pozzolana cement decreased as chemical activator concentration increased;
- From the results obtained in this study, 2% Na_2SO_4 , 3% CaCl_2 or 4% AlCl_3 is considered as the optimum dosage required to accelerate setting times and also improve the early strength development of pozzolana cement;
- The results confirm that chemical activation of pozzolana cements is economically viable as their addition gives similar strengths as OPC at lower cost;

5.2 Recommendations

- For ultimately confirming the conclusions stated, further studies into the examination of the morphology and nature of the generated hydration products as well as the formed microstructure should be undertaken.
- It is also recommended that further research should be conducted into the structural properties of chemically activated concretes since compressive strengths obtained from mortar cubes alone is not enough to make emphatic conclusions.
- To accelerate the setting time and improve the early strength up to or more than the strength of OPC, 30% pozzolana cement should be activated with 2% Na_2SO_4 , 3% CaCl_2 or 4% AlCl_3 .



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