



**SUBSTITUTION OF KAOLIN WITH COAL FLY ASH AS A RAW
MATERIAL FOR THE MANUFACTURE OF CEMENT**

by

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DEDICATION

I dedicate this report to my parents, Mr. and Mrs. Ranjisi, For their encouragement and unwavering support.

ACKNOWLEDGEMENTS

Firstly, and foremost I would like to thank my supervisors, Mrs N.P. Zinyama and Mr M Shumba for their guidance, support, patience, encouragement, generosity, and for the countless ways they helped make this research a success. I wish to extend my gratitude to Dr U Guyo for his guidance, enthusiastic encouragement; useful critiques of this research and helping me keep my progress on schedule.

My humble gratitude goes to Lafarge Cement Zimbabwe and their Laboratory Staff for selflessly providing the requisite guidance and invaluable support that spurred me to greater heights in terms of personal and professional development and making my research a successful one.

Special indebtedness is also due to my family; I thank them for all the support they have given me be it financial, social and valuable contributions. They prepared me to face challenges with faith and humanity.

ABSTRACT

This dissertation investigated the substitution of Kaolin with Coal Fly Ash (CFA) as raw material for the manufacture of cement. The research sought to establish the optimum quantity of CFA, Sand and Limestone required to produce a cement that had improved early day strength and latter strengths of cement due to substitution of kaolin with CFA. This was a novel and creative research where a total of twenty experiments formulated from the central composite design were carried out to investigate the optimum quantities of CFA, Limestone and Sand that is required for the new product. A comprehensive full chemical and physical analysis were carried out under standard conditions to determine the compositions of the raw materials and of the new products formed. From the results that were obtained in this research, CFA and Kaolin chemical analysis showed that it has more aluminium oxide than Kaolin thus it can be used as substitute for kaolin. It was also obtained from the results that CFA plays a major role in the early day strength of cement, with Limestone and Sand playing a major role in the latter day strengths. The optimized results also showed that volumes of CFA of about 32.91% will reach a 2 days' strength of 40.9431Mpa which are better than 14.0000 Mpa that are obtained when Kaolin is used. From the optimized data, it was seen that CFA volumes of 17.05 to 20.30% will produce 2days' cement strength that will be around 30 Mpa on strength and if it is incorporated with Limestone volumes of 84.00 to 85.00% and Sand volumes of 8.80 to 8.90% the latter-day strength will be around 39.0000MPa. These strength results are actually greater than the expected strength of OPC according to the ASTM standards. It was also obtained that CFA plays a major role in the setting time, expansion and water consistency of cement but all the observed results were in the ASTM standards and SAZ range.

DECLARATION

I, Ranjisi Tedia R132235P, hereby declare that I am the sole author of this dissertation. I authorize Midlands State University to lend this dissertation to other institutions or individuals for the purpose of scholarly research.

Signature

Date

APPROVAL

This dissertation entitled, “*Substitution of kaolin with coal fly ash as a raw material for the manufacture of cement*” by..... meets the regulations governing the award of the degree of..... of the Midlands State University, and is approved for its contribution to knowledge and literal presentation.

Supervisor

Date

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Table of List of Abbreviations

CEMENT CHEMISTRY NOTATIONS		
C	Calcium Oxide	CaO
S	Silicon dioxide	SiO ₂
A	Aluminium Oxide	Al ₂ O ₃
F	Iron Oxide	Fe ₂ O ₃
C ₃ S	Alite	3CaO. SiO ₂
C ₂ S	Belite	2CaO. SiO ₂
C ₃ A	Tricalcium Aluminate	3CaO. Al ₂ O ₃
C ₄ AF	Tetracalcium aluminoferrite	4CaO. Al ₂ O ₃ . Fe ₂ O ₃
CA	Calcium aluminate	CaO. Al ₂ O ₃
A/CAC	Alite/Calcium aluminate cement	3CaO. SiO ₂ . CaO. Al ₂ O ₃
CSA	Calcium sulphoaluminate	2CaO. SiO ₂ . Al ₂ O ₃
C ₄ A ₃ S	Tetracalcium sulphoaluminate	4CaO. SO ₃ .Al ₂ O ₃
OPC	Ordinary Portland Cement	
PCC	Portland Composite Cement	
CFA	Coal Fly Ash	

CHAPTER ONE INTRODUCTION

1.1 Background

In Zimbabwe, a substantial volume of CFA is primarily acquired as a by-product of the combustion of coal in power plants. It is expelled from stack emissions by pollution control devices, for example, electrostatic precipitators or fabric filters [1]. CFA which cannot be utilized as a part of some way should be disposed which is costly and conceivably unsafe to the environment [1,2].

Combustion residues are produced in large volumes from coal power plants. The residues incorporate, slag, bottom ash and fly ash, with CFA constituting around seventy percent of the combustion residues [3]. CFA is the segment of the burning deposits that that is not carried away in the flue gas [1,3].

The toxic contents of CFA vary depending on where the coal was mined, CFA ordinarily contains a portion of the world's deadliest toxic heavy metals [4], which are; arsenic, lead, mercury, cadmium, chromium and selenium, and in addition aluminum, antimony, barium, beryllium, boron, chlorine, cobalt, manganese, molybdenum, nickel, thallium, vanadium, and zinc. In places where there is prolonged exposure [5], these toxic metals can cause several types diseases such as cancer, lung disease, respiratory distress, heart damage, kidney disease, gastrointestinal illness, birth defects, reproductive problems, impaired bone growth in children, nervous system impacts, cognitive deficits, developmental delays and behavioral problems [5], [4]. They can likewise damage and kill wildlife, particularly fish and other water-dwelling species [6].

CFA is a pozzolanic material. The utilization of CFA as a substitute of raw materials, admixture or inter-ground decreases energy utilization per ton of product and may increase cement capacity. CFA can also give advantages to the physical and mechanical properties of concrete, for instance it can enhance workability, diminish long term penetrability[2]. Thus, cement manufactures and electric utilities have the chance to work together for a mutual financial and environmental advantage. CFA usage, particularly in cement, has huge environmental advantages, for example, increasing the life of concrete roads and structures by enhancing concrete durability, and greenhouse gas and other antagonistic air emissions [7]. At the point when CFA is utilized to substitute raw materials, for example, kaolin and some limestone, there is diminishment in measure of coal burning products that must be disposed in environment, and they will likewise be preservation of other natural resources and materials. The utilization of CFA has a several advantages which incorporates a decrease in energy utilization, increment in clinker generation and diminishment in carbon dioxide emissions [8].

In a typical cement manufacturing process, silica, aluminium and iron substances are necessary ingredients in cement raw mix. Since CFA is regularly rich in these compounds, it can be utilized as part of cement raw mix, whereas the unburnt carbon in coal fly ash will work as fuel supplement. CFA also contains calcium oxide consequently it can also replace a partial percentages of limestone and this leads to reduced carbon dioxide emissions [9].

1.2 Aim:

- To substitute Kaolin with CFA as a raw material for the manufacture of cement.

1.3 Objectives:

- To sample and characterise CFA, limestone, kaolin and sand.
- To synthesize clinker at different ratios of, CFA, limestone and sand.
- To characterize the synthesized clinker with XRF.
- To produce cement from the clinker synthesized.
- To characterize the produced cement by XRF for chemical properties.
- To investigate the effects of independent parameters on cement quality using response surface methodology.
- To determine physical properties of the produced cement.

1.4 PROBLEM STATEMENT:

CFA toxics have the potential to injure all of the major organ systems, damage physical health and development, and even contribute to mortality in humans[6]. They can also harm and kill wildlife, especially fish and other water-dwelling species [4].Kaolin which is used as raw material in OPC is expensive to obtain and during rainy seasons it hangs and blocks way feeders which leads to production of a raw mix that is not homogenous and this have a negative impact on the burnability of the kiln and produces variations in clinker compositions which will affect the product [14]. Limestone used as the major raw material to OPC is very expensive to obtain as compared to CFA. OPC involves burning of large volumes of limestone thus leading to great emissions of CO₂ in the atmosphere and also may lead to depletion of the ore from the quarry. OPC has greater flux and is produced at higher temperatures of up to 1450°C, thus more fuel is required and this increases production costs [8]. Gel formation in the hydration of C₃S is slower in OPC which means that the early day strengths are weaker thus having a negative impact for construction companies because they will need to wait for days for the strengths to develop before proceeding with their work [13].

1.5 JUSTIFICATION:

Utilization of CFA will reduce pollution problems thereby reducing contamination of the water bodies thus lowering its negative impacts to humans as well as the environment [16]. Kaolin is used to provide alumina to cement and since CFA is rich in alumina it is easy to substitute. Substituting kaolin will reduce mining cost and since CFA does not stick or hang in the way feeders it does not affect the raw mix design and produces no variations in clinker chemistry thus leading to production of good quality cement [17]. CFA will produce a cement that will rely on the hydration of the C_3A and CA to form ettringite, a fiber-like crystal that will develop strength more rapidly and earlier than the OPC during hydration, because gel formation of C_3S is slower than the formation of ettringites [18]. Using CFA will substitute some of the limestone which is a cost reductive method because it is not mined and it also produces green cement because it reduces CO_2 emissions [19]. The unburnt carbon in CFA will lead to reduced fuel consumption thereby reducing costs [20]. The abundance of alumina in CFA promotes liquid phase in clinker production there by providing better brick coat, complete reactions and soft clinker which is easy to grind thereby reducing grinding energy at the cement mills [10].

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

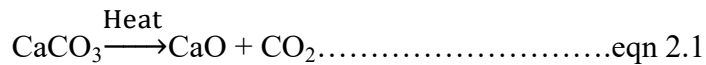
This chapter outlines the chemistry of cement and the effects of cement raw materials (limestone, CFA, sand and kaolin). The chapter also reviews the use of central composite design in the experimental design and highlights on how the X-ray fluorescence (XRF) works, which is a major instrument in cement analysis.

2.1 Introduction to cement

Cement is a material which is highly compatible to the earth's eco-system and most adaptable to sustainable development. Cement is a fine powder which sets after a few hours when mixed with water, thus it is a hydraulic binder and then it hardens into a solid, strong material. Cement is mainly used to bind fine sand and coarse aggregates together in concrete [21].

Cement demand has expanded from 1043 million to 2840 million tons in previous 20 years with fast development coming primarily from the recently industrialized nations like Zimbabwe [22]. Cement production is one of the five most energy intensive industries that consumes about 25% of total world energy and 30– 40% of cement production cost is energy consumption. The energy input comes from the huge energy demand at high temperatures, calcination of CaCO_3 at 850°C and the subsequent clinker formation at 1500°C . Cement production contributes to 5% human made CO_2 . As a calculation base, 1 kg cement releases about 0.8 kg CO_2 that is 50% from the fuel combustion and 50% from the calcination of CaCO_3 [23]. Consequently, as the major influence of industrial revolution, the atmospheric CO_2 has increased by 100 ppm (from 280 to 380 ppm) since the beginning of industrial revolutions in middle 18th century. The CO_2

emissions is a result of coal combustion in the kiln and the de-carbonation of limestone to produce calcium oxide (CaO) in the presence of heat given by the chemical equation:



About 45 percent of CO₂ emissions for cement industry comes from combusting coal which gives the reaction conditions necessary for clinkerisation; 55 percent comes from the limestone dissociation reaction [24].

Cement manufacturing begins at the Quarry where raw materials such as limestone, silica, aluminates, ferric minerals and others are obtained. The rock that is mined usually contains about 80% limestone (which is rich in CaCO₃) and 20% clay or shale (a source of silica, alumina and Fe₂O₃). These are quarried and stored separately. The lime and silica provide the main strength of the cement while the iron reduces the reaction temperatures and gives cement its characteristic grey color[14].

2.2 Cement Raw Materials

2.2.1 Limestone (CaCO₃)

It is composed of calcium carbonate which is a major raw material in the manufacturing of cement. Lime stone is a hard rock that is mined underground. It provides cement with lime which is calcium oxide when exposed to heat and liberates carbon dioxide. All the cementitious compounds are made of lime thus it is the main ingredient of cement. Shortages of lime leads to decrease in the strength of cement and excess free lime (unreacted lime) causes unnecessary expansion and disintegration of the cement [25]. Limestone (CaCO₃) is the primary element of cement, and its percentage is around 60 for every total of the ingredients used. Appropriate percentage of lime which imparts solidifying property ought to be maintained. [26].

2.2.2 Sand (SiO₂)

It is a naturally occurring granular material composed of finely divided rock and mineral particles. It is defined by size, being finer than gravel and coarser than silt. Sand can also refer to a textural class of soil or soil type that is, a soil containing more than 85% sand sized particles (by mass)[22]. The composition of sand varies, depending on the local rock sources and conditions, but the most common constituent of sand in inland continental settings and non-tropical coastal settings such as Zimbabwe is silica (silicon dioxide, or SiO₂), usually in the form of quartz [24]. During the production of cement, silica undergoes chemical reaction with calcium to form dicalcium and tricalcium silicates which are in charge of imparting strength to the concrete. Abundance of silica adds strength to the concrete however its setting time is delayed or prolonged[26].

2.2.3 Kaolin (Al₂O₃)

It is a clay mineral part of the group of industrial minerals. It is mined or found mixed with top soil and mainly it is produced by the chemical weathering of aluminum silicate minerals. In many parts of the world, it is colored pink, orange or red. Kaolin (AS₂H₂, with the oxides represented as A = Al₂O₃, S = SiO₂, H = H₂O) has some binding effects if it is mixed with water thus like CFA it is also a pozzolanic material[15]. Alumina forms complex compounds with silica and calcium to impart setting property to the cement. Larger quantity of alumina quickens setting but weakens the cement[26].

2.2.4 Iron oxide

This ingredient is mainly responsible to impart color to the cement. Ferric oxide helps in the binding of silica and CaO to form calcium silicates, which are compounds of cement which contributes to some of its physical properties[23].

2.2.5 Magnesium oxide

Magnesium oxide (magnesia) also imparts strength to the cement when mixed in small quantity. The existence of MgO can improve the formation of tricalcium silicates, increasing the mechanical property of cement. If in excess, it contributes to the expansion of cement [15].

2.3 Cement Chemistry

Ordinary Portland cement (OPC) clinker is produced by heating a raw mix of limestone, clay or shale, sand and kaolin in a rotary kiln at temperatures of up to 1450°C. Calcium aluminate cement (CAC) is produced by heating a raw mix which contains more alumina and less limestone, and it is also produced at temperatures lesser than OPC of around 1300°C[14].

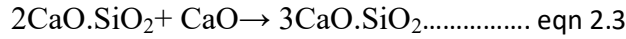
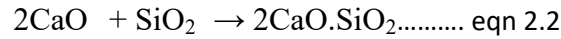
The oxides present in OPC and CAC are shown in table 2.1 below:

Table 2.1: Basic Cement Oxides

C	Calcium Oxide	CaO
S	Silicon dioxide	SiO ₂
A	Aluminium Oxide	Al ₂ O ₃
F	Iron Oxide	Fe ₂ O ₃
	Magnesium Oxide	MgO

[20].

In the kiln the oxides produce the following oxides:



The MgO present in cement remains virtually inert and uncombined.

The kiln feed blend (also called raw meal or raw mix) is adjusted depending on the chemical composition of the raw materials and the type of cement desired through calculations of parameters like:

➤ **Lime Saturation Factor**

The Lime Saturation Factor is a ratio of Calcium Oxide to the other three main oxides applied to clinker, it is calculated as:

$$\text{LSF} = \frac{\text{CaO}}{2.8\text{SiO}_2 + 1.2\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3} \quad [22]$$

➤ **Silica Ratio**

The Silica Ratio (also known as the Silica Modulus) is defined as: $\text{SR} = \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$

A high silica ratio means that more calcium silicates are present in the clinker and less aluminate and ferrite[22].

➤ **Alumina Ratio**

The alumina ratio is defined as: $\text{AR} = \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3}$

This determines the potential relative proportions of aluminate and ferrite phases in the clinker. An increase in clinker AR (also sometimes written as A/F) means there will be proportionally more aluminate and less ferrite in the clinker[15].

Table 2.2: Cementitious Compounds

C_3S	Alite	$3CaO \cdot SiO_2$
C_2S	Belite	$2CaO \cdot SiO_2$
C_3A	Celite	$3CaO \cdot Al_2O_3$
C_4AF	Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
CA	Calcium aluminate	$CaO \cdot Al_2O_3$
A/CAC	Alite/Calcium aluminate cement	$3CaO \cdot SiO_2 \cdot CaO \cdot Al_2O_3$
CSA	Calcium sulphoaluminate	$2CaO \cdot SiO_2 \cdot Al_2O_3$
C_4A_3S	Tetracalcium sulphoaluminate	$4CaO \cdot SO_3 \cdot Al_2O_3$

[22]

2.4 Hydration of cement

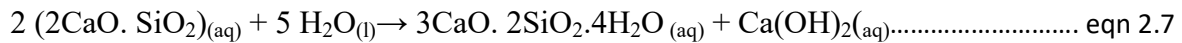
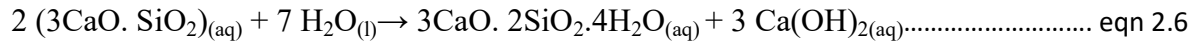
Hydration is the setting and hardening of concrete after cement and water have been added together which results in a change in the physical and chemical properties[23].

Cement hydration has many stages:

- Hydration starts as soon as the cement and water are mixed. The rate of hydration and the heat liberated by the reaction of each compound is different. Each compound produces different products when it hydrates.
- **Tricalcium silicate (C₃S):** This compound hydrates and hardens rapidly and is mainly responsible for initial setting and early strength. Portland cements with higher percentages of C₃S will exhibit higher early strength[27].
- **Tricalcium aluminate (C₃A):** The compound hydrates and hardens quickly and mainly liberates a large amount of heat almost immediately and contributes greatly to early strength. Gypsum is added to Portland cement to retard C₃A hydration. Without gypsum, C₃A hydration would cause Portland cement to set almost immediately after adding water[25].
- **Dicalcium silicate (C₂S):** This compound hydrates and hardens slowly and is largely responsible for strength increases beyond one week[14].
- **Tetracalcium aluminoferrite (C₄AF):** Tetracalcium aluminoferrite hydrates rapidly but contributes very little to strength. Its use allows lower kiln temperatures in Portland cement manufacturing. Most Portland cement color effects are due to C₄AF[27].

2.4.1 Hydration of Silicates (alite and belite)

The hydration of tricalcium silicate and dicalcium silicate give similar chemical products, the difference is only on the amount of calcium hydroxide formed, the heat released and the reaction rate [23].



The primary hydration product is $\text{C}_3\text{S}_2\text{H}_4$, calcium silicate hydrate (C-S-H). It has an amorphous structure making up of poorly organized layers and is called glue gel binder. C-S-H is the material that gives OPC its strength. The hydration of the silicates is not very rapid it happens slowly. Another product produces from the hydration of the silicates is $\text{Ca}(\text{OH})_2$, calcium hydroxide which is a hexagonal crystal. Calcium hydroxide can bring the pH value over 12 and it is good for corrosion protection of steel[27].

2.4.2 Hydration of Tricalcium Alumina (Celite)

C3A reacts very rapidly with water in the absents of gypsum:



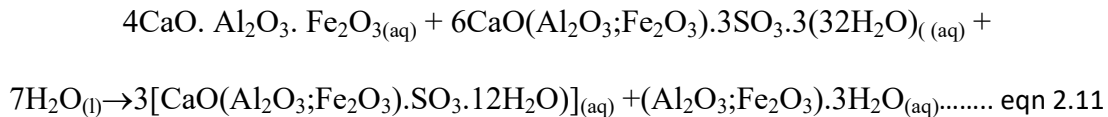
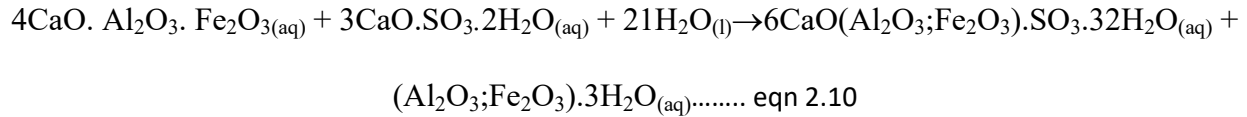
The reaction is so fast that it results in flash set, which is the immediate stiffening after mixing, making proper placing, compacting and finishing impossible[22]. With gypsum, the primary initial reaction of C_3A with water is:



The 6-calcium aluminate trisulfate-32-hydrate is usually called ettringite. The formation of ettringite slows down the hydration of C_3A by creating a diffusion barrier around C_3A . Flash set is thus avoided. Even with gypsum, the formation of ettringite occurs faster than the hydration of the calcium silicates. It therefore contributes to the initial stiffening, setting and early strength development. In normal cement mixes, the ettringite is not stable and will further react to form monosulphate ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 18\text{H}_2\text{O}$)[23].

2.4.3 Hydration of ferrite (C₄AF)

C₄AF forms the same sequence of hydration products as does C₃A, with or without gypsum



The reactions are slower and involve less heat C₄AF never hydrates rapidly enough to cause flash set, and gypsum retards C₄AF hydration even more drastically than it does C₃A [26]. With increase in iron content in C₄AF, hydration of C₄AF becomes slower[22].

2.5 Main factors analyzed on cement

2.5.1 Compressive Strength

The amount of strength produced by a certain cement is due to the amount of C₃S and C₃A present. The greater the amount of the two phases the greater the strength. The C₃A is mainly responsible for early day strength and the C₃S is mainly for later day strengths. OPC contains more C₃S thus it possesses greater later day strengths and CAC contains a lot of calcium aluminates thus it contributes greater early day strengths[28].

2.5.2 Setting Time

Setting refers to a change from a fluid to a rigid stage

Cement + water → cement paste → lose its plasticity gradually → when it loses its plasticity completely → setting occurs[29].

The stages of setting include initial setting time and final setting time. It is important to distinguish setting from hardening, which refers to the gain of strength of a set cement paste. The two first to react are C_3A and C_3S . The setting time of cement decreases with a rise in temperature[23]. Setting time is an important measure in concrete works which is done so as to keep the fresh concrete in the plastic stage for enough time necessary to complete its mixing and placing under practical conditions. But, from the economical side, it is important that the concrete hardens at convenient period after casting[28].

2.5.3 Loss on Ignition (LOI)

LOI is a measure of the percentage of the mass of the material that is lost after leaving the sample of material for one hour in a muffle furnace at a temperature of 950 °C. In terms of limestone, greater LOI means that the limestone contains more calcium carbonate thus it loses carbon dioxide. In terms of cement greater LOI will mean that the cement contains more additives.

LOI (%) will be calculated as follows:

$$\text{LOI} = \frac{(B - C) \times 100}{B - A} [29].$$

A- Mass of empty crucible

B- Initial mass of crucible plus sample before heating.

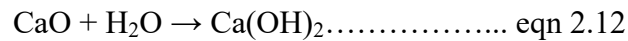
C- Final mass of crucible plus sample after heating.

2.5.4 Soundness (Expansion)

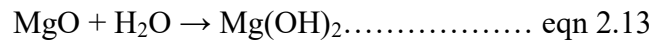
The cement is considered unsound if it undergoes a large change in volume (expansion) that cause cracking of hardened cement paste when it is under condition of restraint.

Causes of expansion

- **Free lime (CaO):** If the raw materials fed into the kiln contain more lime that can combine with the acidic oxides, or if burning or cooling are unsatisfactory, the excess lime will remain in a free condition. This hard-burnt lime hydrates only very slowly and, because slaked lime occupies a larger volume than the original free calcium oxide, expansion takes place. Cements which exhibit this expansion are described as unsound[1].



- **Free MgO:** Cement can also be unsound due to the presence of MgO, which reacts with water in a manner similar to CaO. However, only periclase, that is, 'dead-burnt' crystalline MgO, is deleteriously reactive, and MgO present in glass is harmless, because it hydrates quickly transforming to the stable state in the hardened paste.



Up to about 2 per cent of periclase, (by mass of cement) combines with the main cement compounds, but excess periclase generally causes expansion and can lead to slow disruption[30]

- **Calcium sulfates (gypsum):** If gypsum is present in excess of the amount that can react with C₃A during setting, unsoundness in the form of a slow expansion will result[24].

2.6 Researches on raw material substitution

CFAutilization, especially in concrete, has significant environmental benefits including; increasing the life of concrete roads and structures by improving concrete durability, net reduction in energy use and greenhouse gas and other adverse air emissions. When fly ash is

used in the manufacture of cement there will be reduction in amount of CFA that is disposed in landfills, and they will be conservation of other natural resources and materials [31].

CFA has been successfully used in Portland cement concrete (PCC) as a mineral admixture, and more recently as a component of blended cement, for nearly 60 years [2]. As an admixture, CFA functions as either a partial replacement for, or an addition to, Portland cement and is added directly into ready-mix concrete at the batch plant [2]. Fly ash can also be interground with cement clinker or blended with Portland cement to produce blended cements. ASTM C595 defines two blended cement products in which CFA has been added: 1) Portland-pozzolan cement (Type IP), containing 15 to 40 percent pozzolan, or 2) Pozzolan modified Portland cement (Type I-PM), containing less than 15 percent pozzolan [32].

ASTM C618 defines two classes of CFA for use in concrete: 1) Class F, usually derived from the burning of anthracite or bituminous coal, and 2) Class C, usually derived from the burning of lignite or subbituminous coal. ASTM C618 also delineates requirements for the physical, chemical, and mechanical properties for these two classes of CFA. Class F fly ash is pozzolanic, with little or no cementing value alone. Class C CFA has self-cementing properties as well as pozzolanic properties [26].

In cement manufacturing kaolin is used as a raw material to provide the cement raw mix with aluminum (Al_2O_3) since it is rich in aluminum and due to the fact that CFA is rich in aluminum also it is possible to substitute CFA with kaolin. CFA also contains calcium oxide thus it can also substitute some limestone if it is utilized in cement manufacturing [15].

Research on hybridization of Ordinary Portland Cement (OPC) and calcium sulphoaluminate cements (CSA) presents specific properties and numerous merits [12]. OPC cement synthesized

from limestone and clay achieve high strength through hydration of alite phase to form C-S-H gels but it produces more CO₂ from decomposition of lime at high temperatures of 1350 to 1450°C [13]. Sulphoaluminate cements achieve high strength early due to hydration of C₄A₃S to form ettringites and can be synthesized with less limestone than OPC at slightly lower temperatures of 1250 to 1300°C and generates less CO₂ and they are derived from a mixture of limestone, sand, kaolin and furnace slag [12].

Duvallet [13], synthesized a hybrid alite-calcium sulphoaluminate cement (A/CSA), where raw materials such as hydrated lime, slag, kaolin, bauxite, CFA and red mud were used to produce a hybrid iron-rich A/CSA cement. The cement produced had both properties those of calcium sulphoaluminate cement which relies on the hydration of the Klein's compound C₄A₃S to form ettringites a calcium sulphoaluminate fiber-like crystals, and Portland cement which relies on C₃S to form a gel phase. The iron-rich C₃S-CSA-C₄AF cement produced, required a large amount of iron that can be provided by the use of red mud, which is an abundant by-product from aluminium manufacture. This had reduced cost of A/CSA cements by replacing some of the bauxite, lower the firing temperature (compared to OPC), and emit less CO₂. Finally, it had improved mechanical properties from the combination of C₃A, C₄A₃S and C₄AF phases [13].

The calcium aluminate cement reduces its strength with time, due to a conversion process in which the hydration of the calcium aluminate cement at ambient temperature (<25°C) produces hexagonal hydrated calcium aluminates which are metastable [30]. These therefore inevitably undergo a transformation (conversion) to the cubic form of hydrated calcium aluminate which is the only thermodynamically stable compound. This conversion causes the porosity of concrete made with calcium aluminate cement to increase and therefore reduces its strength. This can take

just a few minutes or several years as the transformation rate depends on several factors, principally temperature. The degree of this reduction in strength can vary [33].

The final strength reached after the conversion can be determined using the test described in UNE EN 14647. Calcium aluminate cement in particular withstands better than Portland cement the action of pure water, sea water, sulfated water and gypsum-bearing soil and also the action of magnesium salts and diluted acids. However, concrete made with this is less resistant to the action of alkaline hydroxides [34,30].

Studies by the Bureau of Reclamation showed that sulfate attack is a two-phased process the first one is Sulfates combine with soluble calcium hydroxide, generated from the hydration of Portland cement, to form calcium sulfate or gypsum. The volume of the resulting gypsum is greater than the sum of its components, causing internal pressures which fracture the concrete[35,36]. The second one is that the Aluminate compounds from Portland cement are attacked by sulfates forming a compound called ettringite. Ettringite formation ruptures the concrete in the same way gypsum formation does [1,7].

The studies by the Bureau of Reclamation proved CFA to be most effective in reducing this deterioration in two important ways, the first one being that the pozzolanic activity of the fly ash binds it to free lime (calcium hydroxide) released in the hydration of Portland cement. The CFA and calcium hydroxide combine in cementitious compounds trapping the calcium hydroxide so that it is no longer available for reaction with sulfates[36]. This prevents the formation of gypsum. The second one being that the cementitious compounds formed when CFA and calcium hydroxide bond block bleed channels and capillary pores in the concrete making it impervious to

aggressive dissolved sulfates. Since the sulfates cannot combine with cement aluminates, ettringite cannot form[37,38].

Studies by the Bureau of Reclamation show that properly proportioned concrete utilizing up to 35 percent CFA will withstand sulfate attack far much better than conventional Portland cement. In all instances, CFA concrete dramatically outperformed conventional Portland cement concrete [39].

2.7 Central composite design

The central composite design (CCD) is an experimental design that can be used in predicting responses. CCD is a widely used for estimating second order response surfaces. It is maybe the most popular class of second order designs. Since it was introduced by Box and Wilson (1951), it has been studied and used by many researchers[40]. Much of the motivation of the CCD evolves from its use in sequential experimentation. It involves the use of a two-level factorial or fraction (resolution V) combined with the following $F=2^k$ or $F=2^{k-p}$ and 2^k axial points and n_0 center points. The sequential nature of the design is quite obvious. The factorial points represent a variance optimal design for a first-order model or a first-order + two-factor interaction type model. The center points clearly provide information about the existence of curvature in the system. If curvature is found in the system, then addition of axial points allows for efficient estimation of the pure quadratic terms[41].

CCD consists of three different design points. The points are the edge points as in two levels designs, star points that take care of the quadratic effects and the centre points. It is made of three variants which are circumscribed (CCC), inscribed (CCI) and face centred (CCF)[40].

2.7.1 CCD variants

2.7.1.1 Circumscribed (CCC)

CCC design is the original central composite design and it does testing at five levels. The edge points (factorial or fractional factorial points) are at the design limits. The star points are at some distance from the centre depending on the number of factors in the design. The star points extend the range outside the low and high settings for all factors. The centre points complete the design. CCC designs provide high quality predictions over the entire design space, but care must be taken when deciding on the factor ranges. Especially, it must be sure that also the star points remain at feasible (reasonable) levels[41].

2.7.1.2 Inscribed (CCI)

In CCI, the star points are set at the design limits (hard limits) and the edge points are inside the range. In a way, a CCI design is a scaled down CCC design. It also results in five levels for each factor. CCI designs use only points within the factor ranges originally specified, so the prediction space is limited compared to the CCC[40].

2.7.1.3 Face centred (CCF)

In this design the star points are at the centre of each face of the factorial space and only three levels are used. Complementing an existing factorial or resolution V design with appropriate star points can also produce this design. CCF designs provide relatively high quality predictions over the entire design range, but poor precision for estimating pure quadratic coefficients. They do not require using points outside the original factor range[40].

After the designed experiment is performed, linear regression is used to obtain results

The CCD design consists of three main sets of experimental runs which are:

- A factorial (perhaps fractional) design in the factors studied, each having two levels;
- A set of *centre points*, experimental runs whose values of each factor are the medians of the values used in the factorial portion. This point is often replicated in order to improve the precision of the experiment;
- A set of *axial points*, experimental runs identical to the centre points except for one factor, which will take on values both below and above the median of the two factorial levels, and typically both outside their range. All factors are varied in this way[41].

2.8 X-ray Fluorescence (XRF) Instrument

XRF is used in determining the chemical elements found in a material, both qualitatively and quantitatively by exposing the material to a primary beam of X-rays. A primary beam of X-rays stimulates the emission of characteristic secondary x-rays from each element present in the sample with intensity proportional to their quantitative concentration as shown in the picture below.[43].

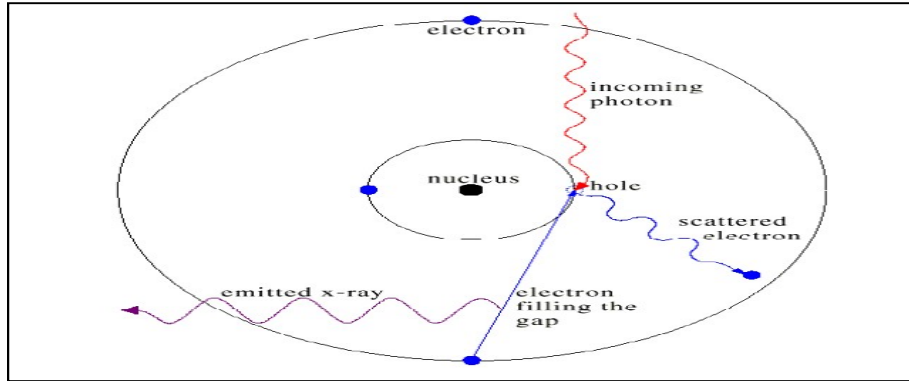


Figure 2.1: A pictorial representation of x-ray fluorescence using a generic atom and generic energy levels. This picture uses the Bohr model of atomic structure and is not to scale[42].

CHAPTER 3 METHODOLOGY

3.0 Introduction

The chapter focuses on the experimental procedures that were done to achieve the aim and objectives of this research.

3.1 Sample Collection

Stratified random sampling, and corning and quartering sampling procedures were used to collect 50.0000kgs, 25.0000kgs and 25.0000kgs of limestone, sand and kaolin respectively from Lafarge Cement Zimbabwe Sternblick Quarry[44]. 50.0000kgs of CFA was collected randomly from Harare Power Company. After collection the samples were stored into airtight containers to avoid contamination.

3.2 Raw Material Analysis

The collected samples that is, sand, CFA, limestone and kaolin were dried in an oven at 110°C for a period of one hour to remove with all the moisture. Limestone in particular was first crushed to 6mm using the laboratory jaw crusher. Limestone, sand and kaolin were then pulverized using a Herzog pulverisor into a fine powder that passed through a 45-micron sieve [29].

- The raw materials were analyzed on their, loss on ignition, chemical analysis and Calorific Value (CV) determination for CFA, before they were used to determine their chemical compositions [29].

3.2.1 Preparation of XRF glass beads using a Fusion machine and analysis using an XRF

0.5000g of sample (sand, CFA, limestone or kaolin) was weighed and mixed with 8.5000g of flux (dilithium tetraborate). The sample plus flux was placed into the platinum crucibles and placed on the fusion machine, producing glass beads [29,45]. The beads were analyzed by the XRF machines for the determination of their chemical compositions [46].

3.2.2 Determination of Loss on Ignition (LOI)

10.0000g of the samples (limestone,CFA, kaolin and sand) was dried in an oven for 30 minutes at 110°C, the sample was then removed and cooled to room temperature in a desiccator. 1.0000g of sample was weighed into the ceramic crucible. The crucible was then placed in the furnace controlled at 950 °C for an hour, removed and cooled. The LOI was determined.

3.2.3 Determination of Calorific Value using a bomb calorimeter

The Dewar was filled with about 450 ml of distilled water and 1.0000g sample (CFA and Coal) was placed on the sample holder that is fixed on the bomb head. A string was then attached on

the ignition wire and made to come in contact with the sample. The sample was bombed and a calorimetric test report, indicating the calorimetric temperature rise, which was fully corrected for all systemic heat leaks, and a heat of combustion value was obtained[47].

3.3 Raw mix design

The central composite design was used to come up with number of runs to be done and their ratios [29]. The number of runs was obtained according the relation $2n+2n+n_c$, where n is the number of factors (threes factors), and n_c is the number of center points (five), and the ratios.

3.3.1 Experimental Domain

The production of the clinker samples was investigated in the experimental domain which followed a Central Composite design shown in table 3.1 below. These are the minimum, median and maximum values of the raw materials used in this research.

Table 3.1: Experimental Domain

	Limestone %	CFA%	Sand %
Min point	70	5	5
Max point	90	40	10
Mid-point	80	22.5	7.5

These values were then used in the design expert software which followed a central composite design. Table 3.2 shows central composites design ratios (20 runs) that were generated from the design expert software.

Table 3.2: Central Composite Design ratios

	Factor 1	Factor 2	Factor 3
Run	A:Limestone%	B:CFA %	C:Sand%
1	85.95	12.09	8.99
2	80.00	5.00	7.50
3	74.05	12.09	8.99
4	80.00	22.50	10.00
5	80.00	22.50	7.50
6	70.00	22.50	7.50
7	80.00	22.50	7.50
8	74.05	12.09	6.01

9	74.05	32.91	8.99
10	85.95	12.09	6.01
11	80.00	40.00	7.50
12	80.00	22.50	7.50
13	80.00	22.50	7.50
14	85.95	32.91	6.01
15	90.00	22.50	7.50
16	80.00	22.50	5.00
17	80.00	22.50	7.50
18	74.05	32.91	6.01
19	85.95	32.91	8.99
20	80.00	22.50	7.50

3.4 Clinker preparation

Distilled water was mixed with the raw mix (composed of Limestone, CFA and sand with respect to table 3.2 above) in the ratio of 1:10 respectively and made into small pellets using a pellet presser. The pellets were placed in a muffle furnace. The temperature was raised to 850°C and it was maintained there for 30 minutes. The temperature was then raised to 1300°C and maintained there for one hour and it was raised to 1450°C for another 30 minutes, the formed clinker was removed and allowed to cool for 30 minutes [13].

- The prepared clinker was analyzed for its chemistry using an XRF.

3.4.1 Preparation of XRF glass beads and analysis

1.0000g of synthesized clinker was weighed and mixed with 8.0000g of flux and placed in the platinum crucible. The platinum crucible was then placed on the fusion machine, which produced the glass beads[48].

3.5 Cement Preparation

The laboratory ball mill was cleaned and a total mass of 5.0000kg was weighed containing 80.00% clinker + 17.00% additive (6mm limestone) + 3.00% gypsum. The 5.0000kg sample was placed into the ball mill and it was milled until 45-micron sieve residues were $\leq 15.00\%$. The cement was collected and stored at room temperature for 24 hours awaiting analysis[3].

3.5.1 Cement analysis

The cement that was produced was analyzed to determine its chemical compositions by preparing XRF beads using a fusion machine and analyzing the glass beads.

3.6 Physical tests procedures

The physical tests were carried out according to standard test procedure approved so as to control the quality of different cements produced corresponding to the clinkers that were produced and understand limitations while interpreting results.

3.6.1 Determination of Water Consistency and Cement setting time

The ground sample was prepared and conditioned together with water for at least 24hrs at a temperature of 22-26°C. The base plate and mold were placed onto the vicat apparatus and the rod with needle was lowered on to the base plate. The indicator was set to rest on 0 mm mark. A cement paste of standard consistency was prepared using 500g of cement and water, a Hobart mixer was used to prepare the paste. The time water was added to the cement was recorded as

zero minutes. The paste was immediately transferred to the Vicat mold, which had previously been placed on a lightly greased base plate, and filled without undue compaction or vibration. The excess cement was removed by gentle sawing motion with a straight-edge implement in such a way as to leave the paste filling the mold and having a smooth upper surface. The filled mold and base plate was placed in the curing cabinet for 15mins. It was transferred to the vicat with a flat surface rod that was about 1 cm in diameter to penetrate vertically into the paste. The scale was checked when penetration had ceased or after 30 seconds after the release of the needle, when the reading on the vicat apparatus was between 5-7mm correct water consistency would have been attained. To determine setting time, the vicat apparatus with the needle was used. The needle is made to penetrate the paste vertically, the depth of the penetration was checked and repeated every 5-10mins bringing the needle into contact with a fresh portion of cement paste in each case. Between each penetration test the specimen was kept in the curing cabinet. When the needle penetrated the paste in the range of 5-7mm depth from the mold bottom, the test was done and the time was recorded [29].

3.6.2 Determination of Strength

For each ISO-mold (3 prisms) one batch of mortar was prepared with the following quantities.

Cement:	450 g \pm 2g
Standard sand:	1350 g \pm 5g
Water:	225g \pm 1g

Prior to dispensing the water, a prepared mold with the hopper in position was centered and firmly clamped in the jolting apparatus. The sand was introduced into the sand hopper on the mixer and water was dispersed into the mixing bowl, the cement was added, immediately the

automatic mixing/dispensing cycle was started by pressing the start button on the process controller. After mixing, the bowl was removed from the mixer.

A scoop was used to add about two layers of mortar (each about 300g) into each of the mold compartments, direct from the mixing bowl. The layer was uniformly spread using the larger spreader, held with its shoulders in contact with the top of the hopper and drawn forwards and backwards once along each of the mold compartments. Then the first mortar layer was compacted using 60 jolts. After 60 jolts the second layer of mortar was introduced and leveled with the smaller spreader and compacted further with 60 jolts. The mold is then lifted from the jolting table and the hopper was then removed and immediately the excess mortar was scrapped off with the metal straightedge. It was then placed without delay on a horizontal base in the curing cabinet with a maintained temperature of 22 – 26 °C and a relative humidity of not less than 90.00 %. Each mold was removed from storage at its appropriate time for demolding (after 24 hours). The demolded specimens were submerged without delay in a curing bath at 22 - 26 °C.

The Toni Tester was used to determine the strength. On the appropriate date and time, the prisms were removed and broken into two halves, one half of the prisms was tested at a time. The average result was recorded [49].

3.6.3 Determination of soundness of cement

A cement paste was prepared using 500g of cement. The time that water was added to the cement was recorded as zero time. Two oiled Le Chatelier molds were filled immediately with the prepared paste by holding the edges of the mold gently together whilst filling. Filled molds were covered with oiled glass plates and a small mass was placed on the plate and the assembly was immersed into water inside the curing room at a temperature of 22 – 26°C. The assembly was removed from the curing room after $24 \pm \frac{1}{2}$ hours and the distance between the ends of the

pointers was measured, in mm and recorded as measurement (A). The Le Chatelier molds with sample was placed into a water bath filled with distilled water and brought to boil and maintained at boiling temperature for 3 hours \pm 5 minutes. The mold with the sample was removed, and the distance between the pointers was immediately measured as (B).

The difference $B - A$ for each specimen was calculated and recorded, the expansion was calculated on the worksheet, expressed as the mean of the two values [50].

3.7 Response Surface Methodology

After all physical tests were carried out; a stepwise regression analysis was carried out on individual parameters to come up with a regression model. The final regression model was obtained after removal of insignificant independent variables [41].

3.7.1 Optimization of the product

The produced data on physical tests was then optimized using CCD to come up with optimum ratios of raw materials of the product.

3.8 Chemical characterization using XRF

In this research X-ray fluorescence spectroscopy (XRF), an analytical technique, was used to determine the chemical elemental constituents in each of the raw materials namely clinker, pilsand, low grade limestone, gypsum and optimised cement test works[42].

Preparation for XRF

- 2 spatulas of Boric acid were placed onto the pelletizer machine (i.e the pellet position).
1 spatula of the sample was then placed on top of the powdered Boric acid. The machine was switched on and after 30 seconds the machine stopped automatically. The machine produced briquettes of 37mm width and 20mm thickness ready for analysis on the XRF machine

CHAPTER 4 RESULTS AND DISCUSSION

4.0 Introduction

The chapter explains the results obtained and their discussions

4.1 Analysis of raw materials

Chemical analysis of the raw materials (Limestone, CFA, Sand and Kaolin) is shown in Table

4.1 below.

Table 4.1: Raw material chemistry

	SiO₂ (%)	Al₂O₃ (%)	Fe₂O₃ (%)	CaO (%)	MgO (%)	SO₃ (%)	Na₂O (%)	K₂O (%)	TiO₂ (%)	P₂O₅ (%)	Mn₂O (%)	L O I (%)
Limestone	8.71	1.7	1.91	45.8	2.21	0.23	0.31	0.18	0.06	0.01	0.6	38.23

CFA	43.07	24.22	17.88	4.66	0.38	1.67	0.75	0.51	1.61	1.59	0.11	16.371
Kaolin	65.98	16.37	5.52	3.01	1.27	0.04	1.41	1.94	0.48	0.08	0.11	4.78
Sand	77.54	7.91	1.62	1.66	0.28	0.11	0.41	3.59	0.3	0.02	0.05	2.47

The calcium oxide content of Limestone of 45.50% showed that the limestone used was high grade [51]. According to international standards limestone with calcium composition exceeding 35 % is regarded as high grade and anything below this can only be used as an additive and not a raw material [29]. CFA was used as a source of alumina in place of kaolin. Table 4.1 shows that CFA has a higher alumina content (24.22 %) compared to kaolin (16.37%) which makes CFA a potential substitute for kaolin in the manufacture of cement. The presence of almost all other components of kaolin in CFA though in inferior quantities further justifies the choice of CFA as a potential substitute of kaolin hence its choice in this work. The values of the LOI are high in Limestone which is due to the loss of CO₂ gas and this also showed that good grade of Limestone was used. CFA loss on ignition is high due to the loss of unburnt carbon and volatile matter [46].

Table 4.2 below shows the calorific values of CFA and Coal.

Table 4.2: Calorific Values (CV)

	CFA	COAL
Mass weighed	1.0051g	1.0052
CV	784.43cal/g	6901cal/g

The CV values obtained are enough evidence that CFA does contain unburnt carbon and it can be used as a fuel supplement in the kiln.

4.2 Experimental Domain

The production of the clinker samples was investigated in the experimental domain which followed a Central Composite design shown in Table 3.1. A total of 20 experiments (Table 3.2) were carried out in the research. In order for consistency checking of the experimental design they were 6 replicate experiments in the 20 test works. The design was used to investigate the key parameters that affect strength, setting time, water consistency and expansion of cement. All the experimental conditions were according to the Central Composite Design (CCD) [41,52].

4.3 Method Error

The validity of the experimental method was established by first running the six replicate experiments. This was done so as to check the consistency of the method which was used in the investigation. The obtained results of the six runs are presented in Table 4.4 below.

Table 4.3: Method error

	2 days' strength (MPa)	7 days' strength (MPa)	28 days' strength (MPa)	48 days' strength (MPa)	Setting time (mins)	Water consistency (%)	Expansion (mm)
Run 1	34.50	41.60	36.70	36.00	131	27.5	5

Run 2	35.10	41.00	36.20	36.10	132	27.6	5
Run 3	34.70	42.10	36.50	36.30	132	27.5	6
Run 4	34.10	41.90	36.50	36.30	134	27.5	5
Run 5	34.50	42.30	36.10	36.20	130	27.6	5
Run 6	34.40	42.00	36.70	36.50	134	27.5	4
Average	34.55	41.82	36.45	36.23	132.17	27.53	5.00
Std	0.33	0.46	0.25	0.18	1.60	0.05	0.63
RSD%	0.96	1.11	0.69	0.48	1.21	0.19	12.65

The relative standard deviation (RSD) was found to be less than 5% in all parameters excluding expansion, showing consistence and reliability of the data hence the method is suitable [41].

4.4 Central Composite Design (CCD)

A multiple regression model that describes a surface model was generated by central composite design. The response surface models describing the variations in the experimental responses were used to establish whether the experimental variables investigated statistically influenced the responses. The designed models can be used to predict the responses at any given level of the independent variables within the experimental domain. The experimental factors used for this investigation and the obtained experimental results are shown in Table 4.5 below.

Table 4.4: Experimental Results

Run	Strength (Mpa)				Setting time (mins)	%Water consistency	Expansion (mm)
	2 days	7 days	28 days	48 days			
1	27.60	35.50	38.10	38.90	137	25.9	4
2	14.00	23.00	34.50	53.80	160	23.5	2
3	25.00	31.00	31.50	31.90	140	26.3	3
4	35.10	42.10	39.30	39.70	134	27.2	5
5	34.50	41.60	36.70	36.00	131	27.5	5
6	31.30	38.10	29.70	29.10	138	27.4	4

7	35.10	41.00	36.20	36.10	132	27.6	5
8	26.10	34.10	32.30	32.10	140	25.1	3
9	41.00	39.00	35.30	30.30	119	27.8	7
10	27.50	34.70	33.50	33.40	137	25.3	3
11	43.00	40.00	34.00	29.00	102	28.3	9
12	34.70	42.10	36.50	36.30	132	27.5	6
13	34.10	41.90	36.50	36.30	134	27.5	5
14	40.90	39.20	33.20	29.10	114	27.0	7
15	35.70	43.60	38.30	38.20	133	26.7	4
16	34.20	42.30	36.60	36.40	138	27.3	7
17	34.50	42.30	36.10	36.20	130	27.6	5
18	38.70	41.30	32.10	31.50	112	28.0	7
19	39.60	42.10	38.40	33.60	117	27.9	6
20	34.40	42.00	36.70	36.50	134	27.5	4

The above table shows the variation in the physical parameters, strength (2, 7, 28 and 48 days), setting time, water consistency and expansion with change in raw material ratios. According to SAZ, ASTM and ISO standards the strength for 2 days' have a standard specification of ≥ 12.0 MPa, 7 days' strength have a standard specification of ≥ 22.5 MPa, 28 days' strength have a standard specification of 32.5 to 52.5 MPa, setting time have a standard specification of > 75 minutes and expansion have a standard specification of ≤ 10 mm [46], [53].

4.4.1 Response surface modelling

4.4.1.1 2days' strength

Model derivation

The general model was proposed to be

$$\text{Strength} = b_0 + b_1A + b_2B + b_3C + b_4A^2 + b_5B^2 + b_6C^2 + b_7AB + b_8AC + b_9BC \dots \text{eqn 4.1}$$

Where *A* is the limestone in %, *B* coal fly ash in % and *C* is sand in %.

A step wise regression analysis in excel as well as in design expert software was carried out to come up with a regression model[54]. The results of the regression analysis are shown in Table 4.6 below.

Table 4.5: 2days strength Anova table

Source	Coefficient	Mean Square	F Value	p-value Prob > F
Model	34.57	56.48	402.04	< 0.0001
<i>A-Limestone</i>	1.15	15.06	107.23	< 0.0001
<i>B-CFA</i>	7.20	322.52	2295.96	< 0.0001
<i>C-Sand</i>	0.37	1.55	11.04	0.0077
<i>AB</i>	-0.84	4.21	29.96	0.0003

<i>AC</i>	-0.74	3.27	23.26	0.0007
<i>A²</i>	-0.39	2.08	14.78	0.0032
<i>B²</i>	-1.31	11.98	85.30	< 0.0001
<i>Std. Dev.</i>	0.37	<i>R-Squared</i>	0.9965	
<i>Mean</i>	34.83	<i>Adj R-Squared</i>	0.9940	
<i>C.V. %</i>	1.08	<i>Pred R-Squared</i>	0.9809	
<i>PRESS</i>	7.59	<i>Adeq Precision</i>	72.730	

There is only a 0.01% chance that an F-value this large could occur due to noise. Values of Prob>F are less than 0.0500 which indicates that model terms are significant. In this case A, B, C, AB, AC, A², B² are significant model terms. The Pred R-Squared of 0.9809 is in reasonable agreement with the Adj R-Squared of 0.9940; that is the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 72.7300 indicates an adequate signal. This model can be used to navigate the design space.

The final regression model equation after removal of all insignificant independent variables was as follows:

$$2\text{days strength} = 34.57 + 1.15A + 7.20B + 0.37C - 0.84AB - 0.74AC - 0.39A^2 - 1.31B^2 \dots \text{eqn 4.2}$$

Although it appears that the model fits the data well, it is of great importance to run a lack of fit test and perform a residual analysis before accepting this model as a good description of the data.

Model Validation

On validating the model, the following were done:

Normal probability plot

Normal probability plot: is used to test the normality of a set of data. Some formal tests such as chi-squared tests can be used as well. The normal probability plot graphs the quantiles of the data to be tested against the corresponding quantiles of a theoretical normal distribution with the same mean and standard deviation. These plots are produced by a statistical program.

The models validity was tested by the inspection of the normality of the residuals. This was obtained by creating a normal probability graph. The data that is normally distributed should be close to the straight line and scattered randomly around it.

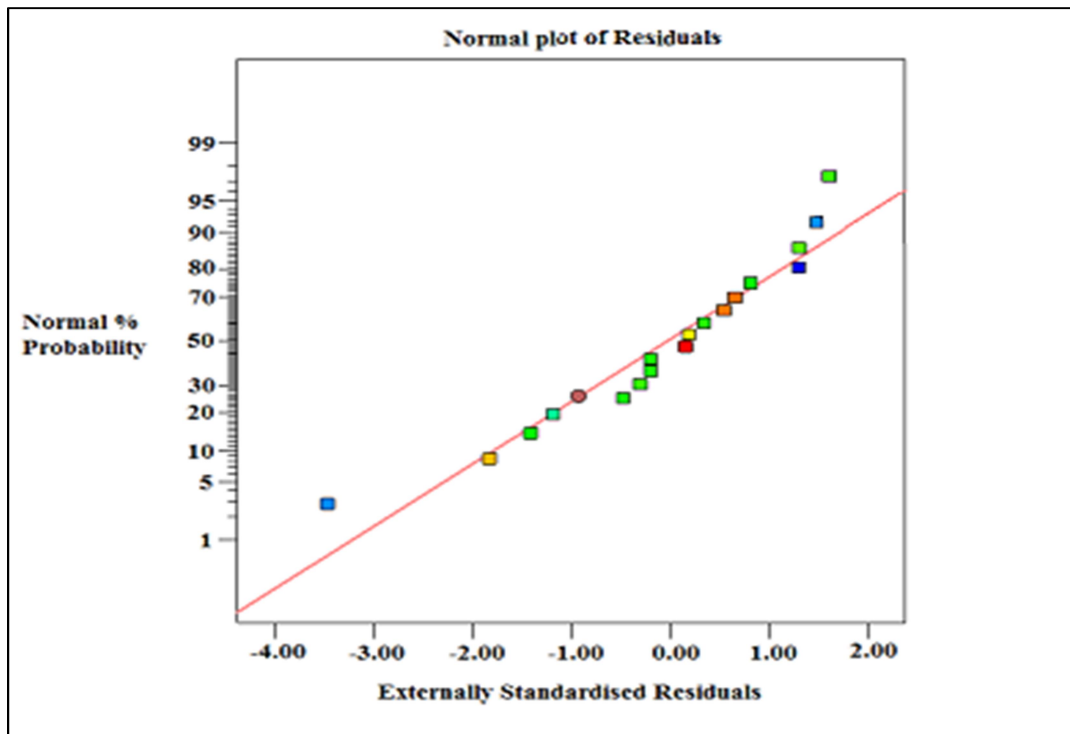


Figure 4.1: Normal probability plot of 2days' strength residuals

From the normal probability plot in Figure 4.1, the residuals are close to the straight line and are scattered around it with no particular pattern. In conclusion the data is normally distributed and thus it is suitable for modelling.

Check for outliers

Central composite design was used to check for outliers (fig 4.2) and none were found, showing the statistical validity of the surface model. This is determined by no points beyond the border lines around ± 4.0 of the externally standardised residuals (fig 4.2).

Standard residuals versus predicted

A plot of standard residuals versus predicted values is useful in testing the distribution of the residuals. The distribution of residuals is determined by a plot of standard residuals versus predicted values.

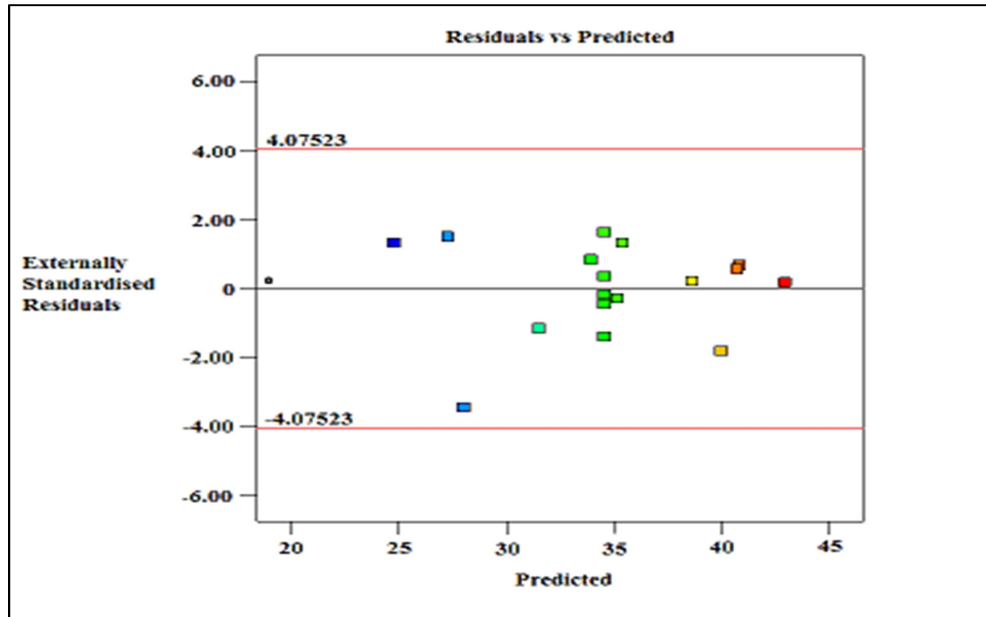


Figure 4.2: Graph of standard residuals vs predicted percentages for 2 days' strength

From the graph in Figure 4.2, the residuals are randomly distributed around zero with no observable pattern. There is no indication that the residuals are dependent on each other. There is also no indication of large differences in variation between the residuals. Standard residuals are randomly distributed around zero with no particular pattern, showing statistical validity of the log model [41].

3D response surface plot

The 3D surface plot is used to compare the relationship between two factors and a parameter such as strength are related.

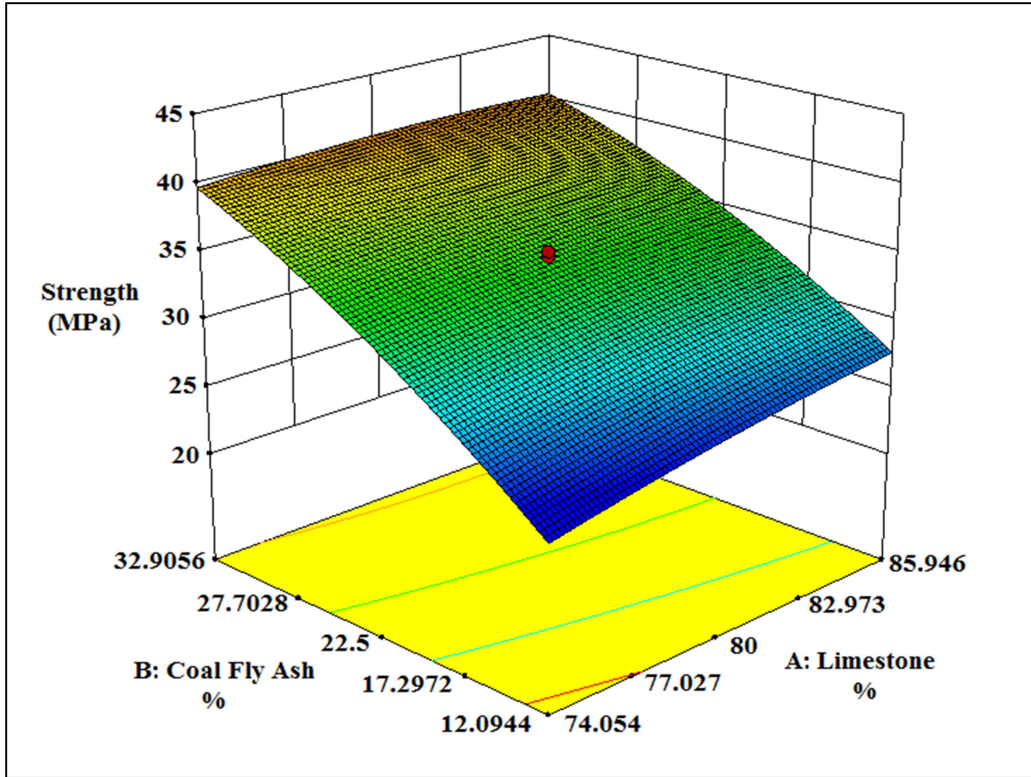


Figure 4.3: 3D Surface Plot of 2days (Limestone vs Coal Fly Ash)

From the plot above, it can be seen that the strength rapidly increases with an increase in CFA (%) - B as well as a slight increase with the increase in limestone (%) - A. This shows that CFA has a greater effect on the early day strength of cement than limestone because the high Al_2O_3 in CFA promotes the formation of alumina compounds which plays a major role in early day strength. The obtained experimental results fit the expected results [55].

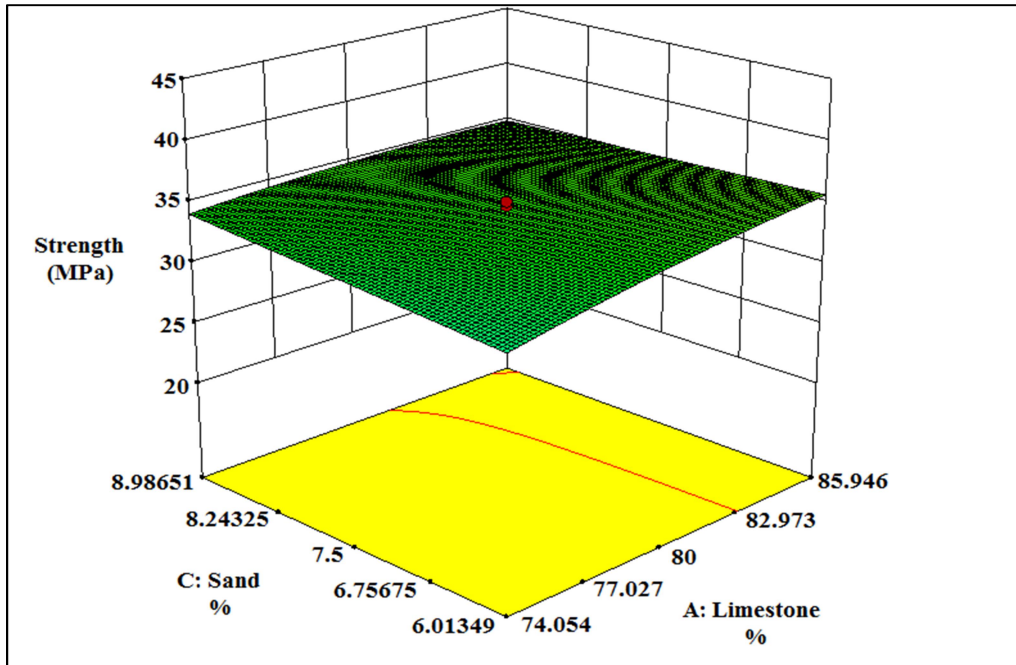


Figure 4.4: 3D Surface Plot of 2days' strength (Limestone vs Sand)

From the plot above, it can be seen that the strength does not increase with an increase sand (%) - C as well as a slight increase with the increase in limestone (%) - A, this is because these two are important in the formation of silicate phases, which forms by gel formation which is a slow process [23].

4.4.1.2 7 days' strength

Model derivation

The general model which was proposed in equation 4.1 above was fitted to the observed effect on the 7 days' strength. Table 4.7 below shows a summary of results after a stepwise regression analysis and the elimination of insignificant terms as computed by design expert software.

Table 4.6: 7days strength Anova Table

Source	Coefficient	Mean Square	F Value	p-value Prob > F
Model	41.94	67.79	137.52	< 0.0001
<i>A-Limestone</i>	1.12	17.25	34.99	0.0001
<i>B-CFA</i>	3.35	102.10	207.12	< 0.0001
<i>C-Sand</i>	-0.15	0.30	0.62	0.4489
<i>AB</i>	-0.51	2.10	4.26	0.0634
<i>AC</i>	1.13	10.35	21.00	0.0008
<i>A²</i>	-0.33	1.56	3.16	0.1032
<i>B²</i>	-4.60	178.87	362.85	< 0.0001
<i>Std. Dev.</i>	0.70	<i>R-Squared</i>		0.9887
<i>Mean</i>	38.78	<i>Adj R-Squared</i>		0.9815
<i>C.V. %</i>	1.81	<i>Pred R-Squared</i>		0.9418
<i>PRESS</i>	27.91	<i>Adeq Precision</i>		42.997

The R^2 value of 0.9887 was obtained meaning that 98.87% of the variation in the observed effect on the 7 days' strength is explained by the model [54]. The Model F-value of 137.52 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of Prob > F less than 0.0500 indicate model terms are significant. In this case A, B,

AC, B² are significant model terms. The Pred R-Squared of 0.9418 is in reasonable agreement with the Adj R-Squared of 0.9815, that is the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The experimental ratio of 42.9970 indicated an adequate signal. This model can be used to navigate the design space.

The final regression model equation after removal of all insignificant independent variables was as follows:

$$7 \text{ days' strength} = 41.94 + 1.12A + 3.35B - 0.15C - 0.51C + 1.13AC - 0.33A^2 - 4.60B^2 \dots \text{eqn}$$

4.3

Normal probability plot

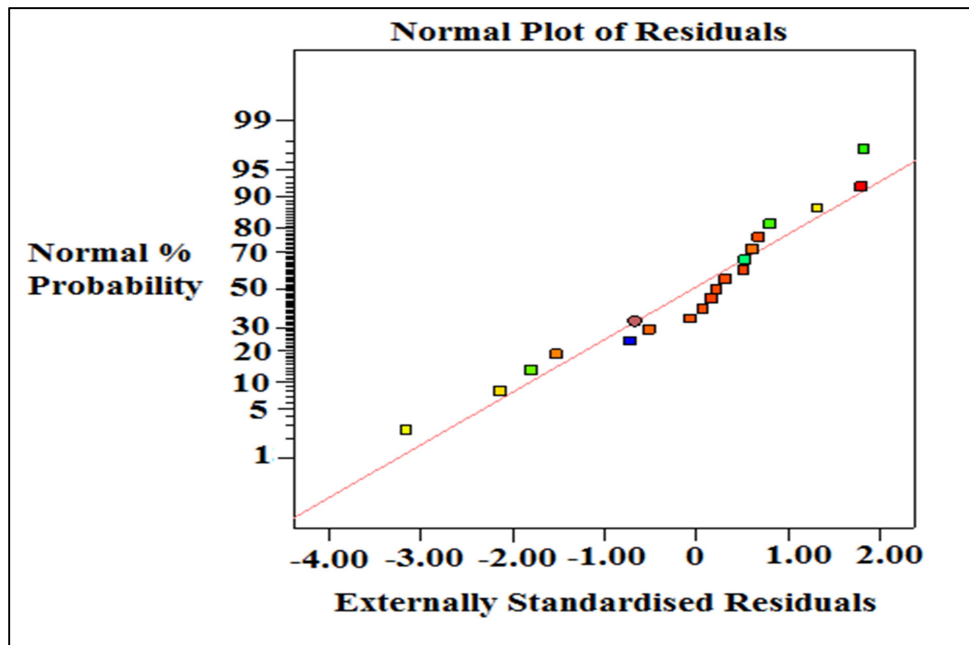


Figure 4.5: Normal plot of 7 days' strength

Figure 4.5 is a plot of the normal probability of the effect on 7 days' strength residuals. It shows no particular pattern and are scattered close to the line thus showing the normality of the data

Standard residuals versus predicted

Figure 4.6 below shows a plot of standard residuals (predicted minus observed) versus predicted 7 days' strength values.

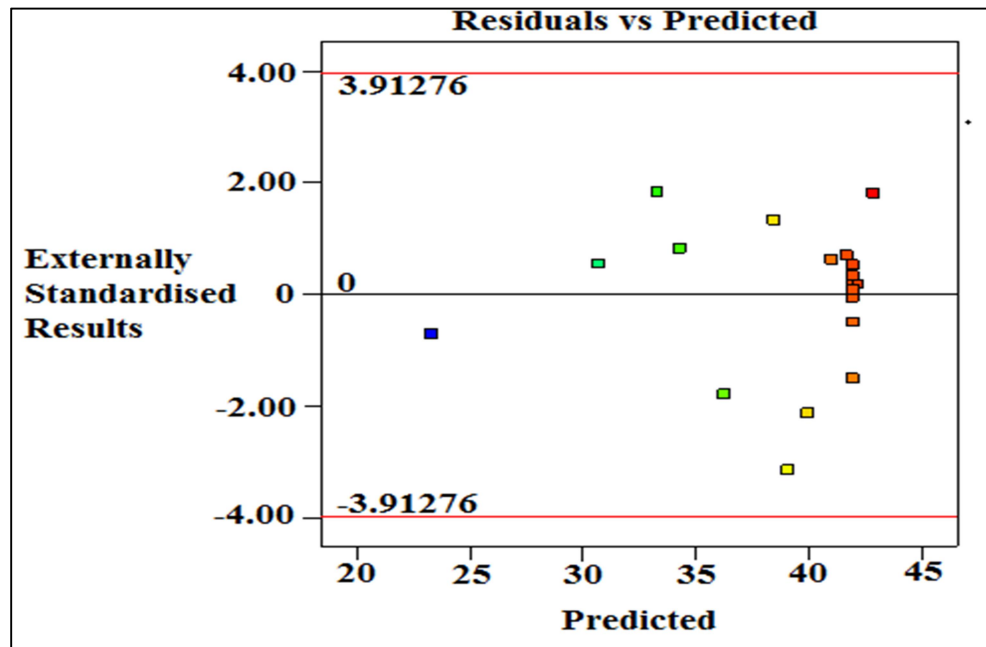


Figure 4.6: Graph of standard residuals vs predicted percentages for 7 days' strength

The standard residuals are randomly distributed around zero with no particular pattern. There are no outliers showing validity of the model [41]. This is determined by no points beyond the border lines ± 4.0 of externally standardised residuals.

3D surface plot

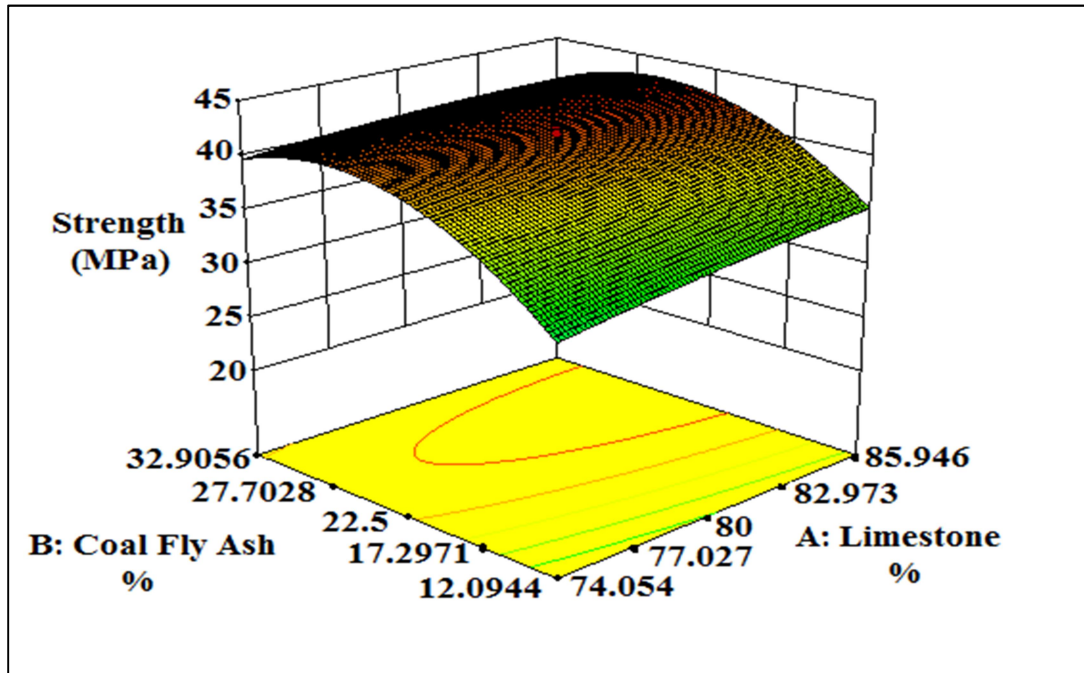


Figure 4.7: 3D Surface Plot of 7days (Limestone vs CFA)

From the plot, it can be seen that the strength rapidly increases with an increase in CFA (%) up to around 27% and it slightly decreases this is due to conversion from metastable crystalline substance to stable crystalline substance of the ettringite crystal. The stable crystals formed after conversion occupy a lesser volume than the metastable and this causes the concrete material to become porous thus reducing strength. The stable crystals do not hold water so water is released and this makes the concrete soft thereby reducing strength. The plot also shows a slight increase with the increase in limestone (%) due to a slow formation of silicate phases. The plot also shows that CFA is independent of Limestone in the formation of strength[56].

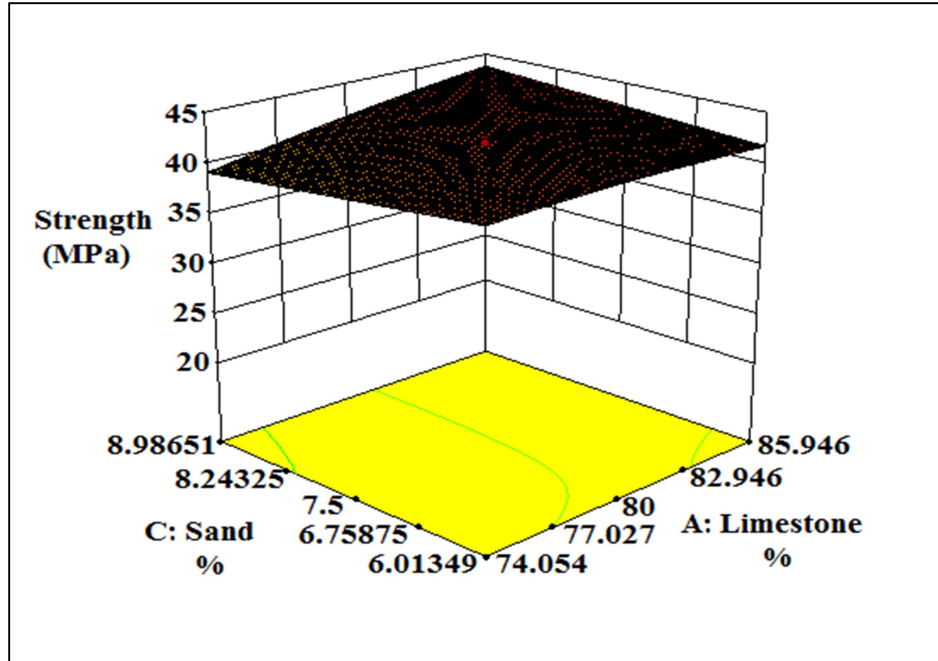


Figure 4.8: 3D Surface Plot of 7days (Limestone vs Sand)

From the plot, it can be seen that the strength does not increase with an increase sand (%) - C as well as a slight increase with the increase in limestone (%) - A. This is because silicates phases form slowly. The plot shows that limestone and sand are dependent because strength increase with an increase in both limestone and sand because these two forms calcium silicate phases which are useful in strength. The obtained experimental results fit the expected results [12].

4.4.1.3 28 days' strength

Model derivation

The general model which was proposed in equation 4.1 above was fitted to the observed effect on the 28 days' strength. Table below shows a summary of results after a stepwise regression analysis and the elimination of insignificant terms as computed by design expert software.

Table 4.7: 28days strength Anova Table

Source	Coefficient	Mean Square	F Value	p-value Prob > F
Model	36.74	18.32	13.65	< 0.0001
<i>A-Limestone</i>	1.94	51.27	38.18	< 0.0001
<i>B-CFA</i>	0.20	0.56	0.42	0.5305
<i>C-Sand</i>	1.22	20.53	15.29	0.0018
<i>AC</i>	0.92	6.84	5.10	0.0418
<i>A²</i>	-1.12	18.12	13.50	0.0028
<i>B²</i>	-1.03	15.36	11.44	0.0049
<i>Std. Dev.</i>	1.16	<i>R-Squared</i>		0.8630
<i>Mean</i>	35.27	<i>Adj R-Squared</i>		0.7997
<i>C.V. %</i>	3.28	<i>Pred R-Squared</i>		0.5536
<i>PRESS</i>	56.86	<i>Adeq Precision</i>		12.487

The R^2 value of 0.8630 was obtained meaning that 86.30% of the variation in the observed effect on the 28 days' strength is explained by the model [13]. The Model F-value of 13.65 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of Prob > F less than 0.0500 indicate that the model terms are significant. In this experiment A, C, AC, A^2 , B^2 are significant model terms. The Pred R-Squared of 0.5536 is not as close to the Adj R-Squared of 0.7997 as normally expected, that is the difference is more than

0.2. This may indicate a large block effect or the rearrangement caused by ettringite crystals [57]. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The experimental ratio was 12.4870 which indicated an adequate signal. This model can be used to navigate the design space. The final regression model equation after removal of all insignificant independent variables was as follows:

$$28\text{days strength} = 36.74 + 1.94A + 0.20B + 1.22C + 0.92AC - 1.12 A^2 - 1.03B^2 \dots\dots \text{eqn 4.4}$$

Normal probability plot

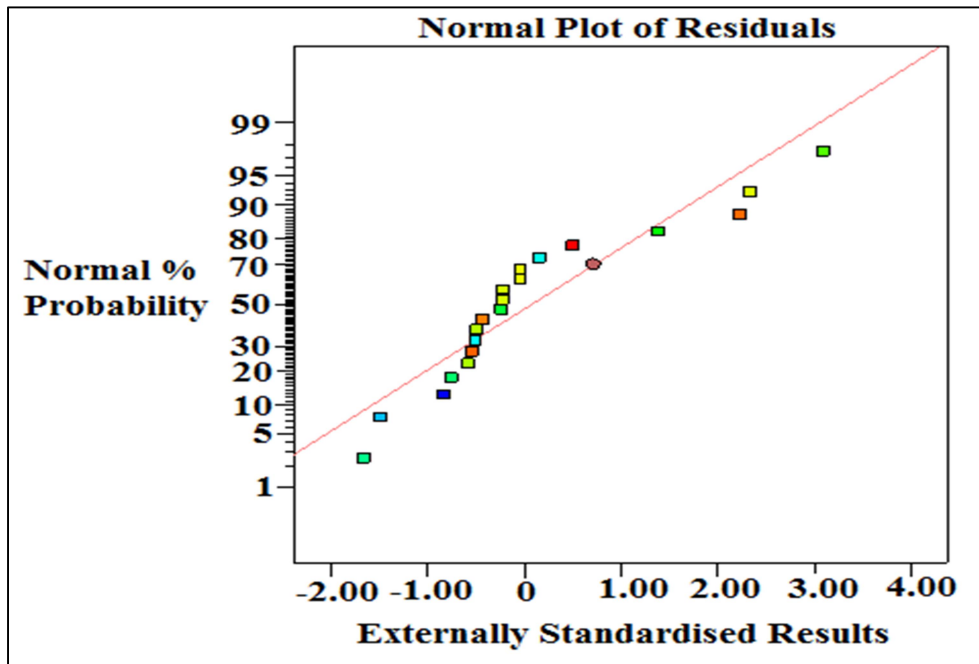


Figure 4.9: Normal plot of 28 days' strength

Figure 4.9 is a plot of the normal probability of the effect on 28 days' strength residuals shows no particular pattern and are scattered close to the line thus showing the normality of the data.

Standard residuals versus predicted

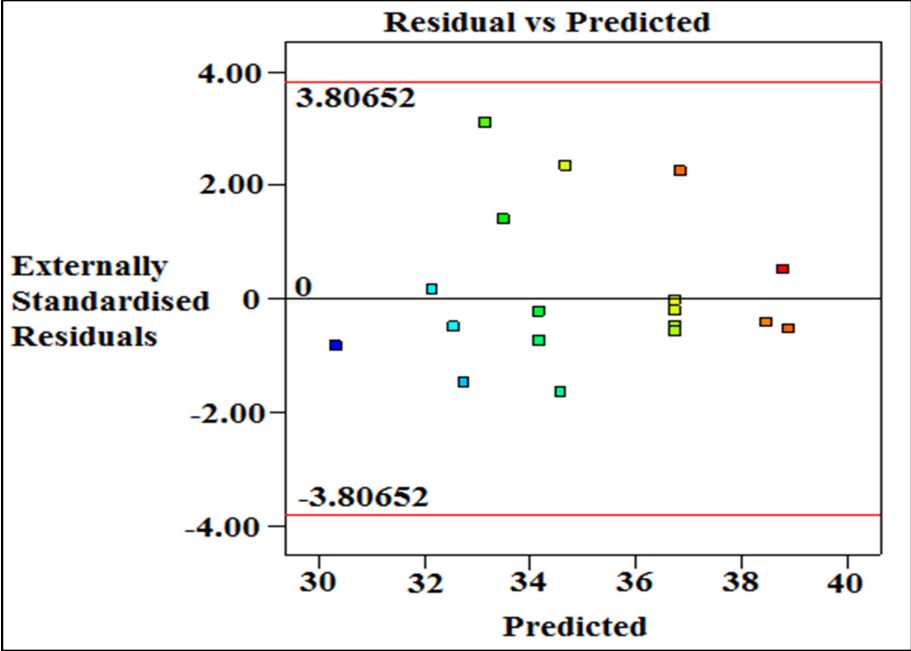


Figure 4.10: Graph of standard residuals vs predicted percentages for 28 days’ strength

The standard residuals are randomly distributed around zero with no particular pattern. There are no outliers showing validity of the model. This is determined by no points beyond the border lines ± 4.0 of externally standardised residuals.

3D surface plot

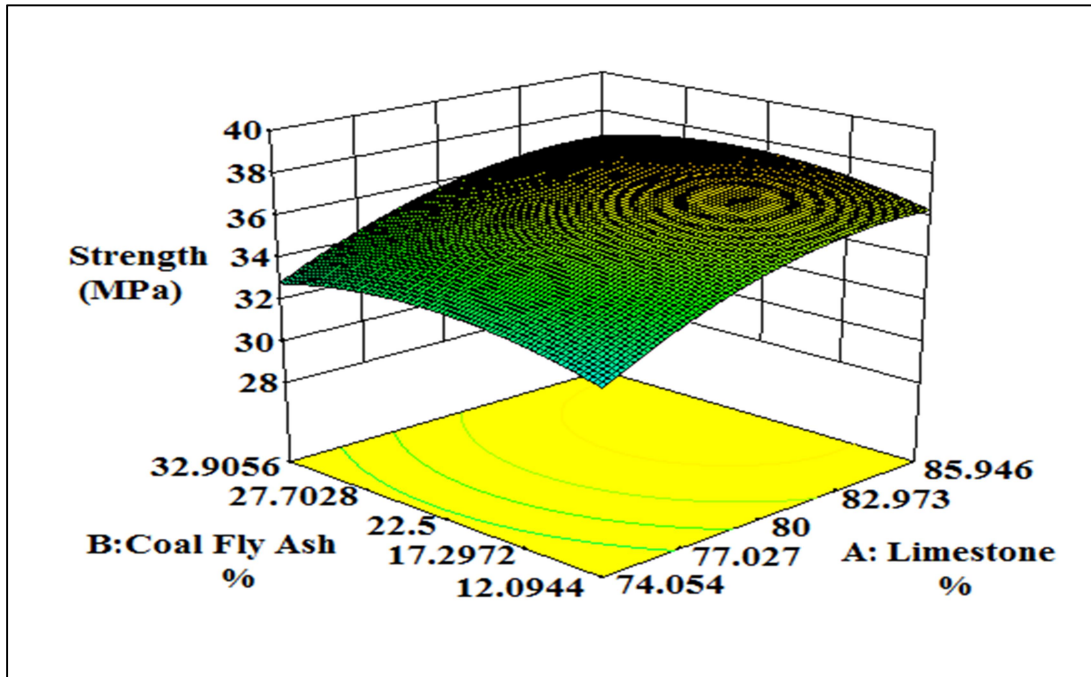


Figure 4.11 3D Surface Plot of 28days (Limestone vs CFA)

From the plot, it can be seen that the strength increases with an increase in CFA (%) - B up to around 22.50% and it slightly decreases because if more CFA is used they will be greater rearrangement which leads to a decrease in strength during the later days [57]. The plot also shows an increase in strength with an increase in limestone (%) - A, because it plays a major role in later day strength which is also in agreement with literature [11].

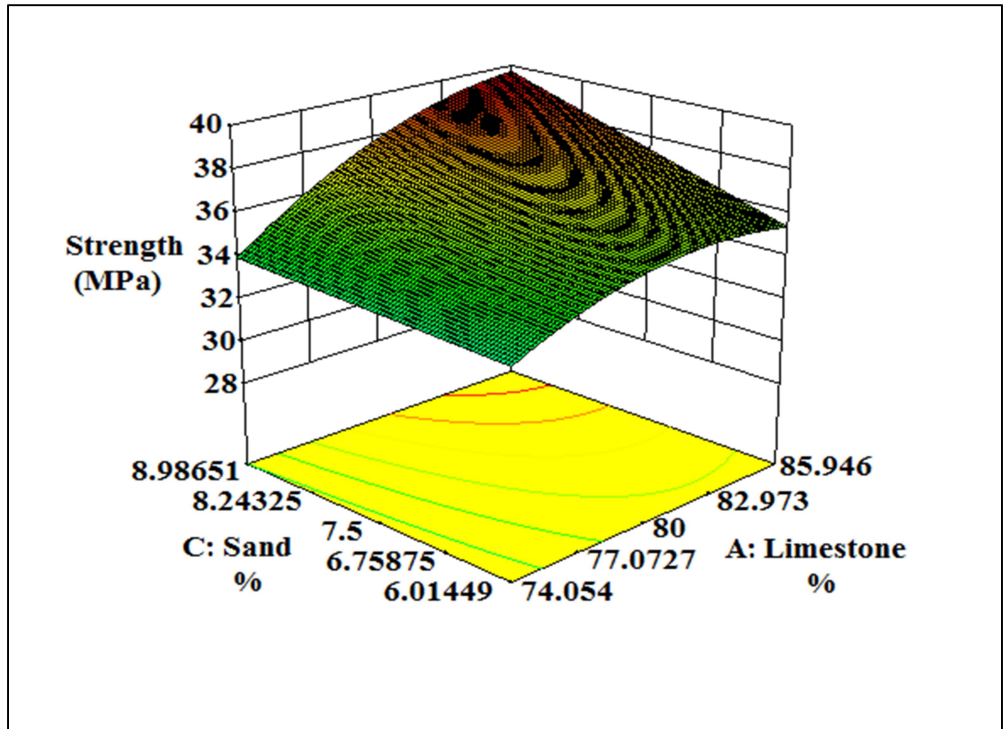


Figure 4.12 3D Surface Plot of 28days (Limestone vs Sand)

From the plot, it can be seen that the strength slightly increases with an increase in sand (%) - C as well as an increase in limestone (%) - A. This is because both sand and limestone are involved in the formation of silicate phases which plays a major role in the strength of cement during the later days. The plot shows that there is a great increase in strength as we increase both parameters because the silicate phases would have been formed. The slight decrease due to greater volumes of Limestone could have been due to the unreacted calcium oxide or all the silica would have reacted to form the silicate phases, so excess limestone does not aid in strength.

4.4.1.4 48 days' strength

Model derivation

The general model which was proposed in equation 4.1 above was fitted to the observed effect on the 48 days' strength. Table below shows a summary of results after a stepwise regression analysis and the elimination of insignificant terms as computed by design expert software [40].

Table 4.8: 48days strength Anova Table

Source	Coefficient	Mean	F	p-value
	Estimate	Square	Value	Prob > F
Model	36.25	24.01	122.62	< 0.0001
<i>A-Limestone</i>	1.04	9.51	48.57	< 0.0001
<i>B-CFA</i>	-1.37	16.35	83.53	< 0.0001
<i>C-Sand</i>	1.03	14.66	74.89	< 0.0001
<i>AB</i>	-0.92	6.85	34.96	0.0002
<i>AC</i>	1.42	16.24	82.97	< 0.0001
<i>A²</i>	-2.09	32.68	166.90	< 0.0001
<i>B²</i>	-1.93	27.90	142.50	< 0.0001
<i>C²</i>	0.55	3.99	20.40	0.0015
<i>Std. Dev.</i>	0.44	<i>R-Squared</i>		0.9909
<i>Mean</i>	34.02	<i>Adj R-Squared</i>		0.9828
<i>C.V. %</i>	1.30	<i>Pred R-Squared</i>		0.9079
<i>PRESS</i>	17.85	<i>Adeq Precision</i>		35.292

The R^2 value of 0.9909 was obtained meaning that 99.09% of the variation in the observed effect on the 28 days' strength is explained by the model. The Model F-value of 122.62 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of Prob > F less than 0.0500 indicate model terms are significant. In this experiment A, B, C, AB, AC, A^2 , B^2 , C^2 are significant model terms. The Pred R-Squared of 0.9079 is in reasonable agreement with the Adj R-Squared of 0.9828 that is the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 35.2920 obtained indicates an adequate signal. This model can be used to navigate the design space. The final regression model equation after removal of all insignificant independent variables was as follows:

$$48\text{-day strength} = 36.25 + 1.04A - 1.37 B + 1.03C - 0.92AB + 1.42AC - 2.09A^2 - 1.93B^2 + 0.55C^2 \dots\dots\dots \text{eqn 4.5}$$

Normal probability plot

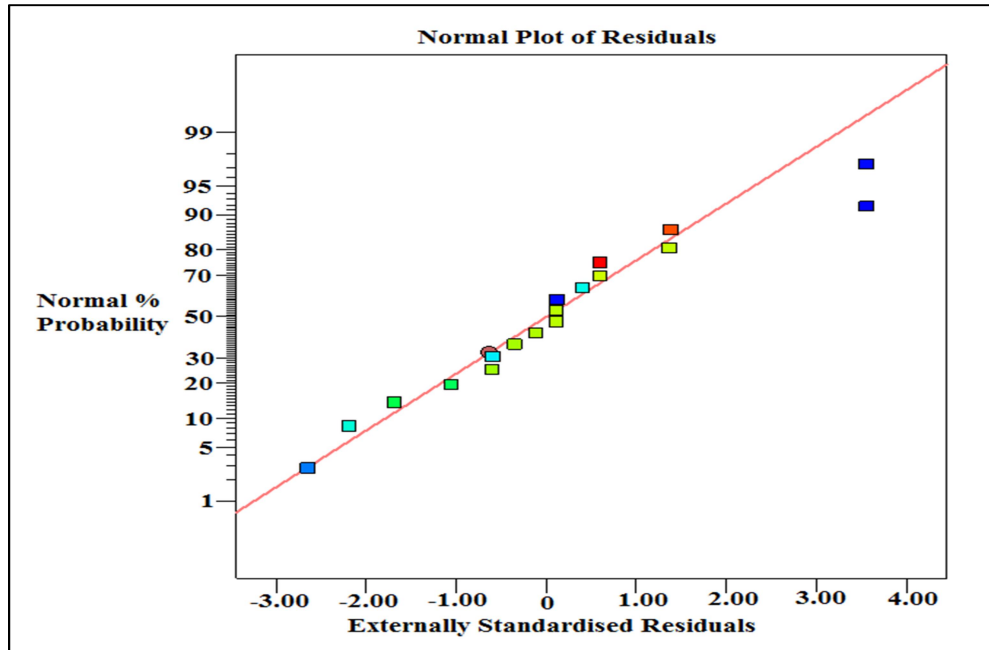


Figure 4.13: Normal plot of 48 days' strength

Figure 4.13 is a plot of the normal probability of the effect on 48 days' strength residuals shows no particular pattern and are scattered close to the line thus showing the normality of the data.

Standard residuals versus predicted

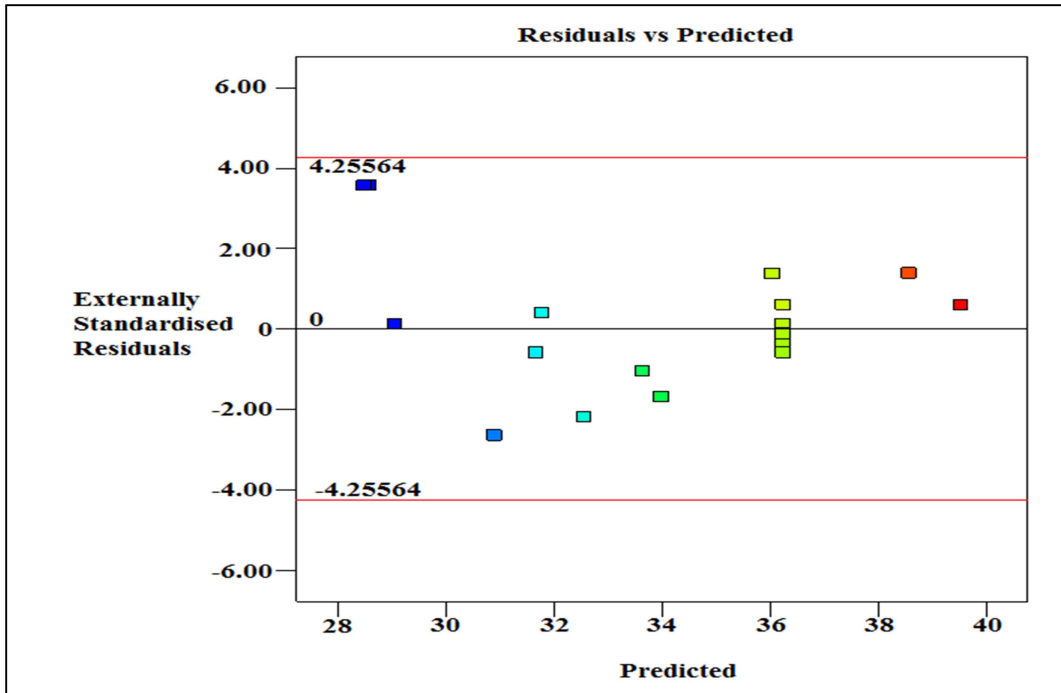


Figure 4.14: Graph of standard residuals vs predicted percentages for 48 days' strength

The standard residuals are randomly distributed around zero with no particular pattern. There are no outliers showing validity of the model. This is determined by no points beyond the border lines ± 4.0 of externally standardised residuals.

3D surface plot

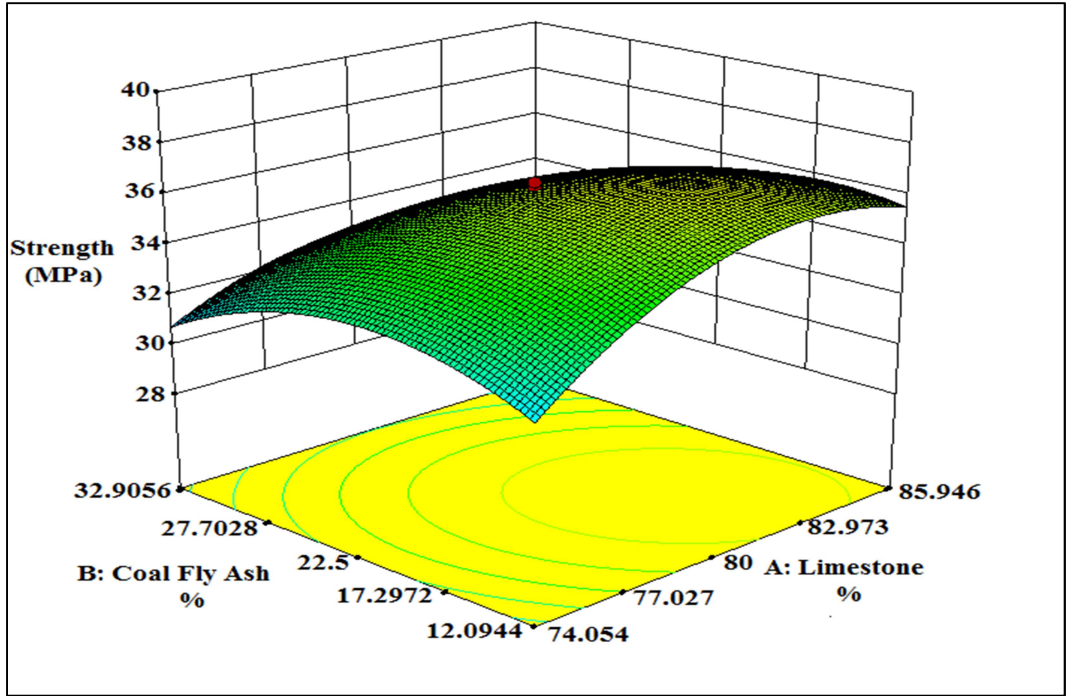


Figure 4.15: 3D Surface Plot of 48days (CFA Vs Limestone)

From the plot, it can be seen that the strength increases with an increase in CFA (%) - B up to around 22.50% and it decreases due to rearrangement which leads to a decrease in strength during the latter days [36]. The plot also shows a greater increase in strength with an increase in limestone (%) - A. This is because it plays a major role in the latter day strength where the silicate phases would have been formed which is also in agreement with literature [23]. The slight decrease due to greater volumes of Limestone could have been due to the unreacted calcium oxide or all the silica would have reacted to form the silicate phases, so excess limestone does not aid in strength.

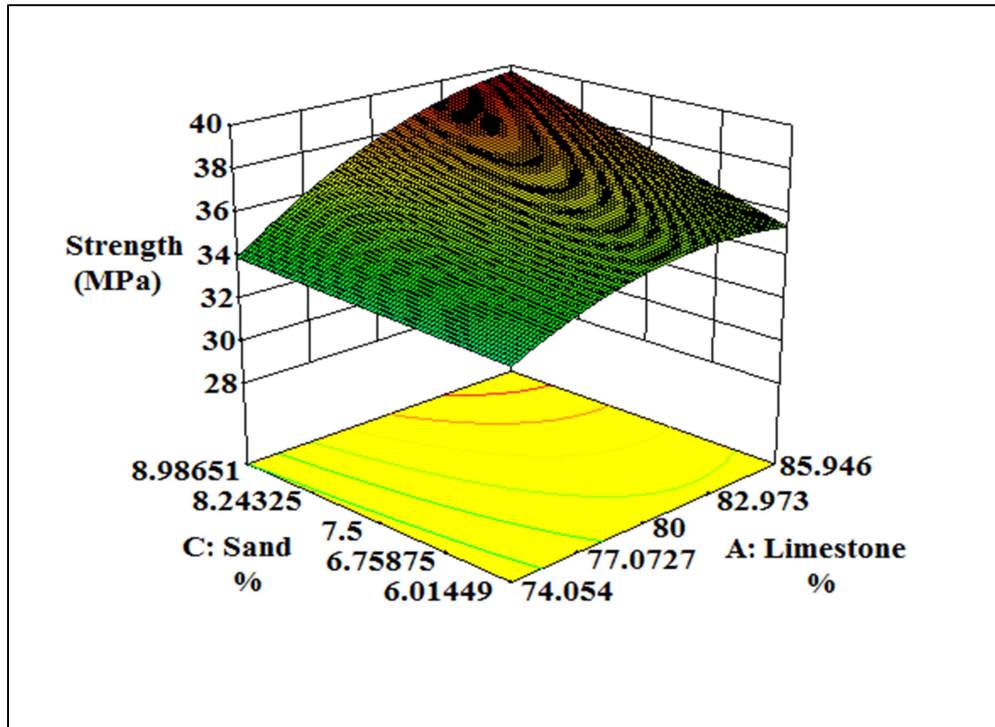


Figure 4.16: 3D Surface Plot of 48days (Sand Vs CFA)

From the plot, it can be seen that the strength slightly increases with an increase in sand (%) - C as well as an increase with an increase in limestone (%) - A. This is because both sand and limestone are involved in the formation of silicate phases which plays a major role in the strength of cement during the latter days. The plot shows that there is a great increase in strength as we increase both parameters because the silicate phases would have been formed. The slight decrease due to greater volumes of Limestone could have been due to the unreacted calcium oxide or all the silica would have reacted to form the silicate phases, so excess limestone does not aid in strength.

Trend analysis of strength

From the above results obtained on the strength analysis it was seen that CFA plays a major role in the early day strength of cement this is due to the fact that alumina compounds forms rapidly

during the early days and they so by formation of ettringite crystals[36]. During the later days the rearrangement of the ettringite crystals causes the strength to reduce. Limestone and sand proved to be weak in the early day strength of cement but having a greater effect during the latter day strength of cement, this is because gel formation is a slower thus providing strength during the later days after the gels had formed[13].

4.4.1.5 Effect on setting time

The general proposed model (equation 4.1) was fitted to the observed effect on setting time. Table 4.7 shows a summary of results after a stepwise regression analysis and removal of insignificant terms as computed by design expert software.

Table 4.9: Setting time Anova table

Source	Coefficient	Mean	F	p-value
	Estimate	Square	Value	Prob > F
Model	36.25	676.72	99.15	< 0.0001
<i>A-Limestone</i>	1.04	15.20	2.23	0.1564
<i>B- CFA</i>	-1.37	1114.72	163.32	< 0.0001
<i>B²</i>	-1.93	240.27	35.20	< 0.0001
<i>Std. Dev.</i>	2.61	<i>R-Squared</i>		0.9520
<i>Mean</i>	129.16	<i>Adj R-Squared</i>		0.9424
<i>C.V. %</i>	2.02	<i>Pred R-Squared</i>		0.9141
<i>PRESS</i>	183.26	<i>Adeq Precision</i>		33.597

The Model F-value of 99.15 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of Prob> F less than 0.0500 indicate model terms are significant. In this case B, B² are significant model terms. The Pred R-Squared of 0.9141 is in reasonable agreement with the Adj R-Squared of 0.9424 that is the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The obtained ratio of 33.5970 indicates an adequate signal. This model can be used to navigate the design space. The final regression model equation after removal of all insignificant independent variables was obtained to be:

$$\text{Setting Time} = 133.17 - 1.05A - 11.00B - 5.32B^2 \dots \dots \text{eqn 4.6}$$

Normal probability plot

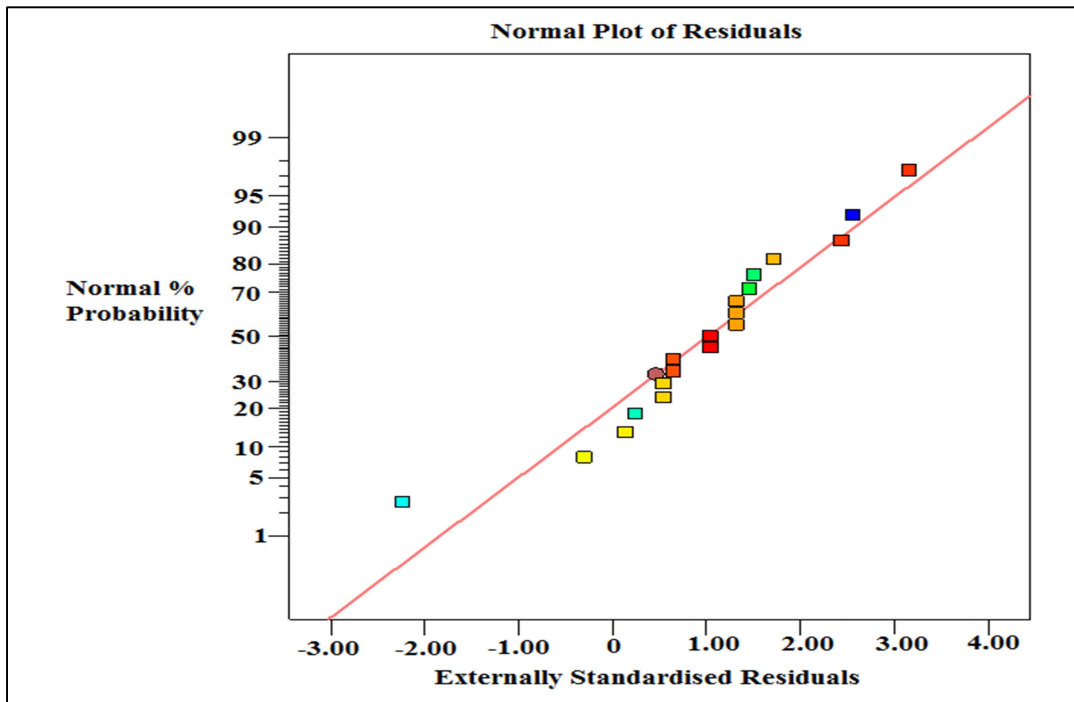


Figure 4.17: Normal Plot of Setting Time

The normal probability plot of the effect on Setting time residuals shows no particular pattern showing normality of the data Figure 4.17 and they are scattered close to the line.

Residuals versus predicted

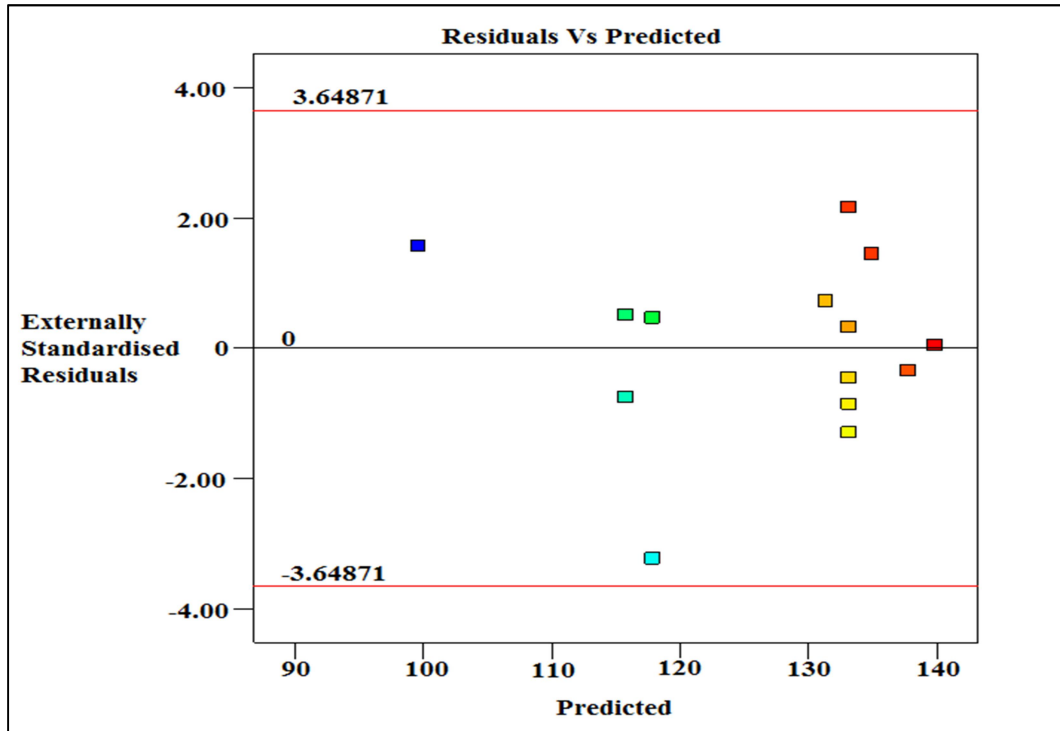


Figure 4.18: A graph of Standard Residuals Vs Predicted of Setting Time

The standard residuals are randomly distributed around zero with no particular pattern. There are no outliers showing validity of the model[40]. This is determined by no points beyond the border lines around ± 4.0 of externally standardised residuals.

3D Surface plot

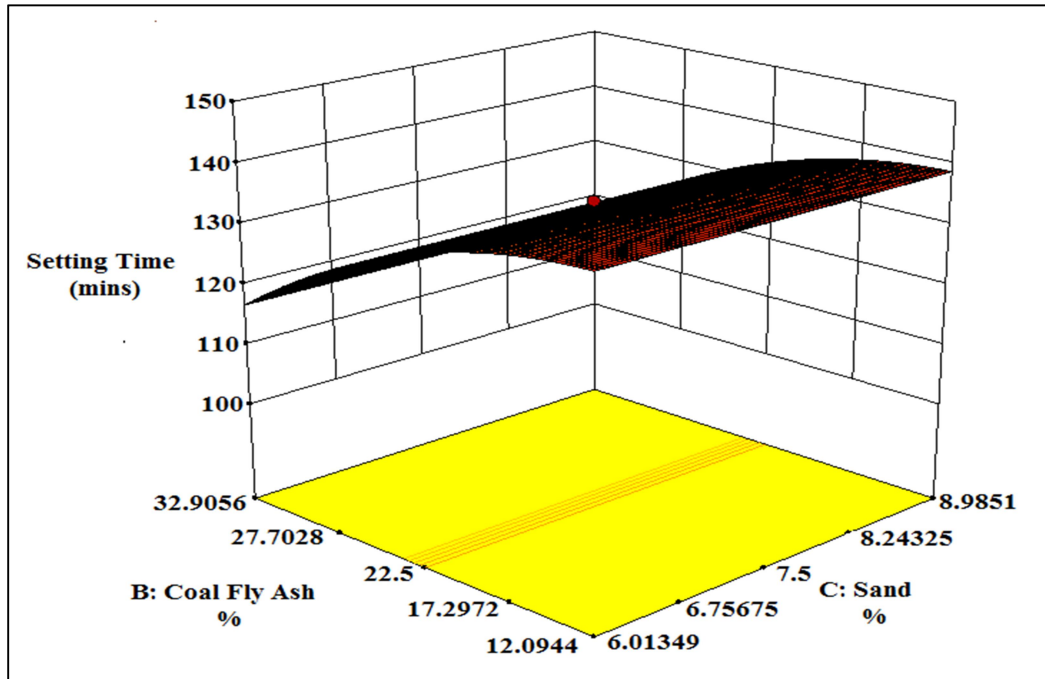


Figure 4.19: 3D Surface plot of the effect of CFA Vs Sand on setting time.

Figure 4.19 showed that an increase in sand has no significant effect in the setting time of cement. As we increase the CFA the clinker became soft which made the cement finer when it was ground and since fineness is inversely proportional to setting time, this explains the reduction in setting with an increase in CFA[56]. The plot also shows that the two parameters are independent of each other in terms of setting time.

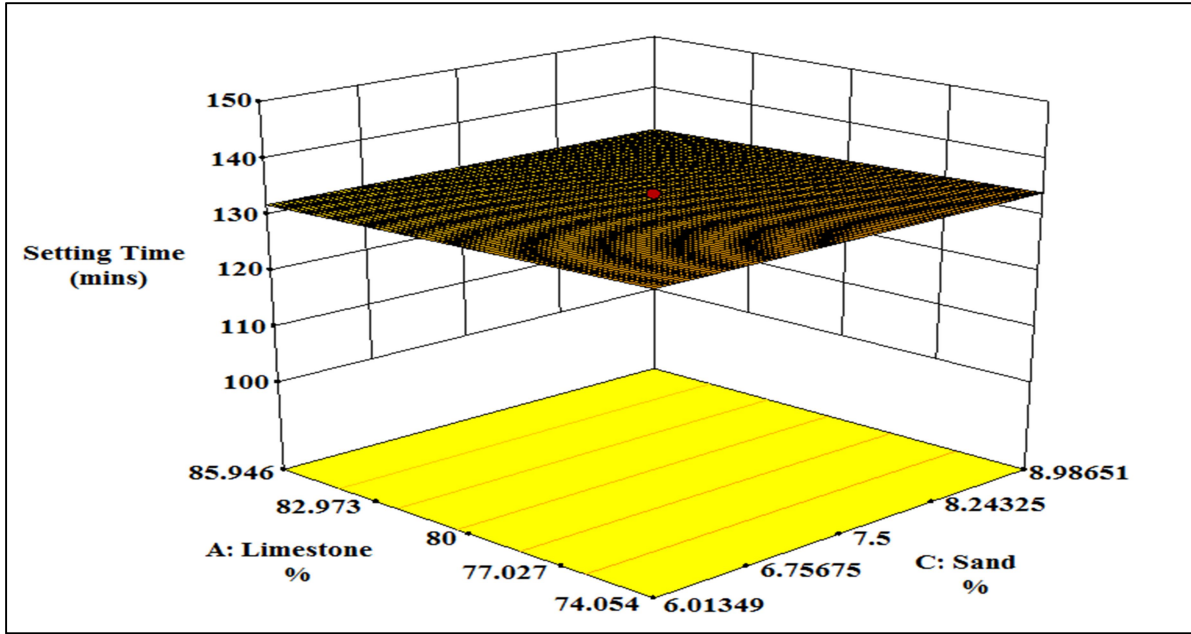


Figure 4.20: 3D Surface plot of the effect of Limestone Vs Sand on setting time.

Trend analysis for setting time

The above results showed that CFA has a greater influence on setting time as compared to limestone and sand, this is because the more the CFA the greater the fines of cement making the cement more reactive thus reducing the setting time of cement, the other reason is that CFA provides alumina to cement and the alumina hydrates very fast to form ettringite crystals as the heat of hydration is very high, thus this reduces the setting time of cement[27]. Setting time is a measure of the time required for the cement to harden and this information on setting time shows that CFA plays a major role in the hardening of cement in the early days[23].

4.4.1.6 Effect on expansion

The general model which was proposed in equation 4.1 above was fitted to the observed effect on expansion. Table 4.11 below shows a summary of results after a stepwise regression analysis and the elimination of insignificant terms as computed by design expert software.

Table 4.10: Expansion Anova table

Source	Coefficient		F Value	p-value Prob > F
	Estimate	Mean Square		
Model	5.35	17.12	36.16	< 0.0001
<i>A-Limestone</i>	0.000	0.000	0.000	1.0000
<i>B-CFA</i>	1.89	48.63	102.70	< 0.0001
<i>A²</i>	-0.43	2.74	5.78	0.0287
<i>Std. Dev.</i>	0.69	<i>R-Squared</i>		0.8715
<i>Mean</i>	5.05	<i>Adj R-Squared</i>		0.8474
<i>C.V. %</i>	13.63	<i>Pred R-Squared</i>		0.8305
<i>PRESS</i>	9.99	<i>Adeq Precision</i>		20.620

The R^2 value of 0.8715 was obtained meaning that 87.15% of the variation in the observed effect on expansion is explained by the model. The Model F-value of 36.16 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of Prob > F less than 0.0500 indicate model terms are significant. In this case B, A^2 are

significant model terms. The Pred R-Squared of 0.8305 is in reasonable agreement with the Adj R-Squared of 0.8474 that is the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The experimental ratio of 20.6200 indicates an adequate signal. This model can be used to navigate the design space. The final regression model equation after removal of all insignificant independent variables was as follows:

$$\text{Expansion} = 5.35 + 0A + 1.89B - 0.43A^2 \dots\dots\dots \text{eqn 4.7}$$

Normal probability plot

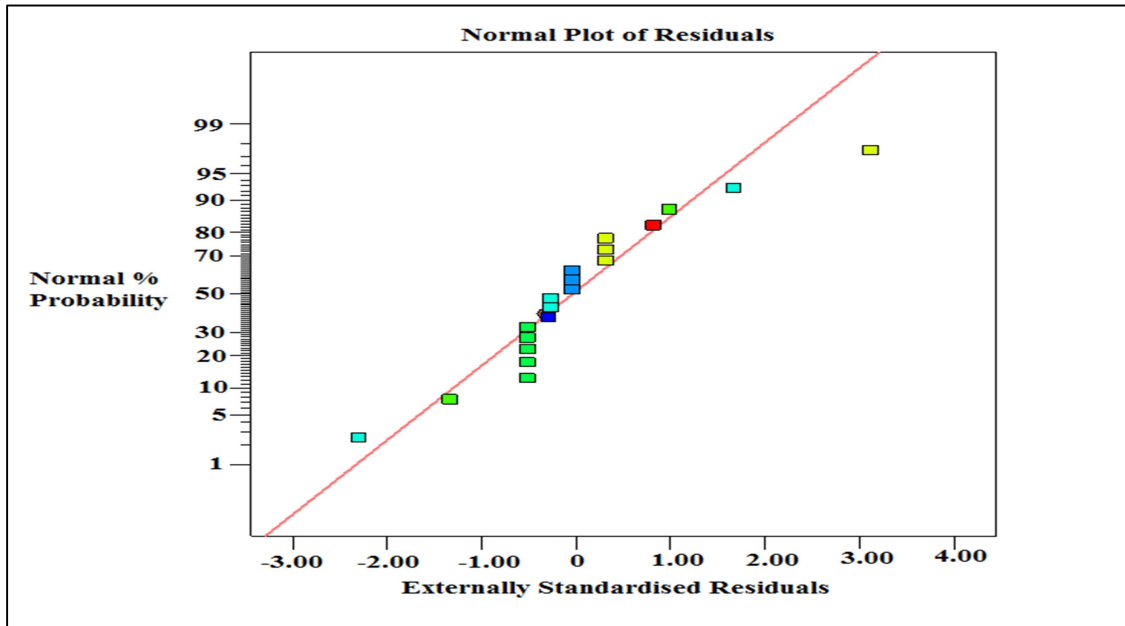


Figure 4.21: Normal Plot of Expansion

Figure 4.21 is a normal probability plot of the effect on expansion residuals shows no particular pattern showing normality of the data.

Residual versus predicted

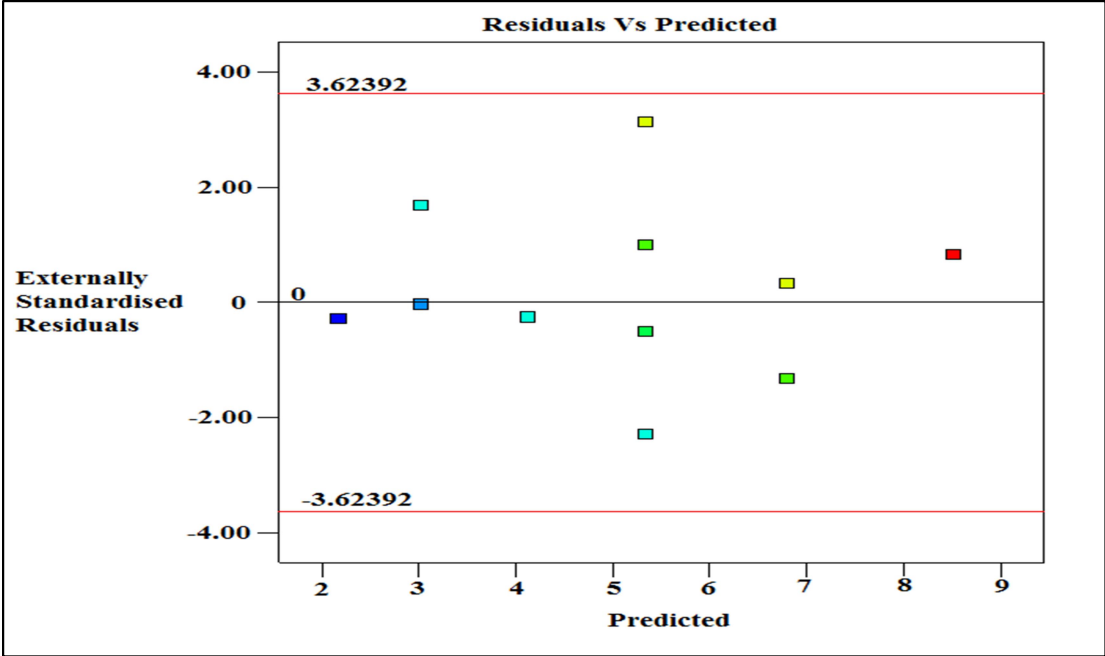


Figure 4.22: A graph of Standard Residuals Vs Predicted of Expansion.

The standard residuals are randomly distributed around zero with no particular pattern. There are no outliers showing validity of the model. This is determined by no points beyond the border lines around ± 4.0 of externally standardised residuals.

3D Surface Plot

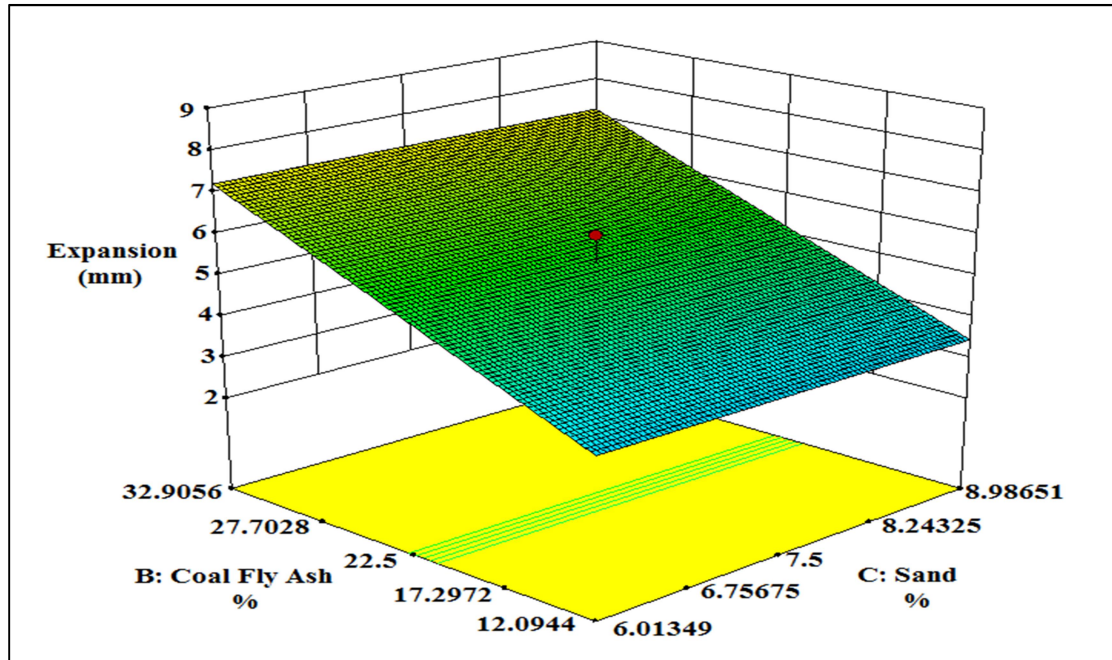


Figure 4.23: 3D Surface plot of the effect of CFA Vs Sand on Expansion.

From the plot above an increase in expansion with an increase in CFA, this is due to the fact that expansion is directly proportional to alumina in cement because it is the first compound to be formed and it forms ettringite crystals which are greater in volume and as we increase the CFA the alumina increases thus increasing expansion [58], but the expansion caused by CFA was within the acceptable limits of cement expansion according to literature [29]. It can also be observed from the plot that an increase in sand does not affect expansion.

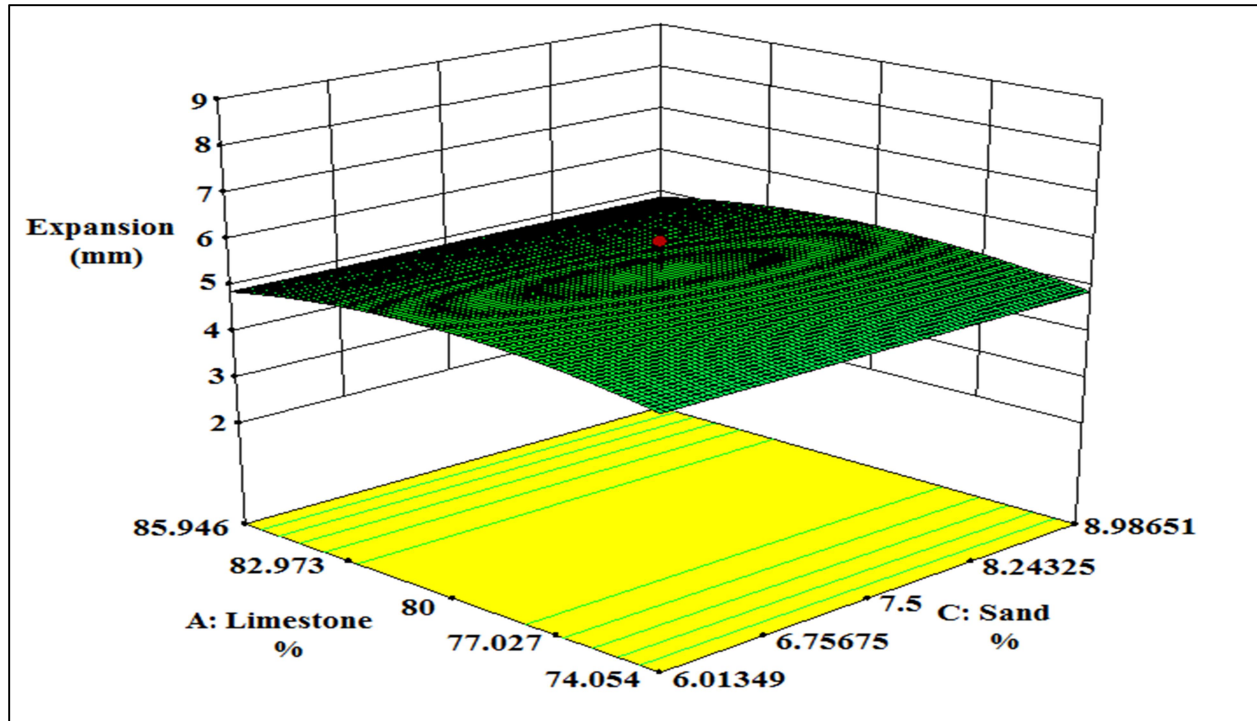


Figure 4.24: 3D Surface plot of the effect of Limestone Vs Sand on Expansion.

Figure 4.24 is a 3D surface plot which shows that an increase in both limestone and sand has no significant effect on the expansion of the cement.[48].

Trend analysis

The above mentioned results showed that CFA has a greater effect on the expansion of cement as compared to other parameters this is because the alumina compounds reacts faster than silica compounds.

4.4.1.7 Effect on water consistency

The general model which was proposed in equation 4.1 above was fitted to the observed effect on water consistency. Table 4.12 below shows a summary of results after a stepwise regression analysis and the elimination of insignificant terms as computed by design expert software.

Table 11: Water Consistency Anova table

Source	Coefficient	Mean	F	p-value
	Estimate	Square	Value	Prob > F
Model	27.33	11.85	68.80	< 0.0001
<i>B-CFA</i>	1.18	19.15	111.18	< 0.0001
<i>A²</i>	-0.56	4.55	26.42	< 0.0001
<i>Std. Dev.</i>	0.42	<i>R-Squared</i>		0.8900
<i>Mean</i>	26.95	<i>Adj R-Squared</i>		0.8771
<i>C.V. %</i>	1.54	<i>Pred R-Squared</i>		0.7998
<i>PRESS</i>	5.33	<i>Adeq Precision</i>		26.086

The R² value of 0.8900 was obtained meaning that 89.00% of the variation in the observed effect on water consistency is explained by the model [54]. The Model F-value of 68.80 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of Prob > F less than 0.0500 indicate model terms are significant. In this case B, B² are significant model terms. The Pred R-Squared of 0.7998 is in reasonable agreement with the Adj R-Squared of 0.8771 that is the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The experimental ratio of 26.0860 indicates an adequate signal. This model can be used to navigate the design space. The final regression model equation after removal of all insignificant independent variables is as follows:

$$\% \text{ Water Consistency} = 27.33 + 1.18B - 0.56B^2 \dots \dots \text{eqn 4.8}$$

Normal probability plot

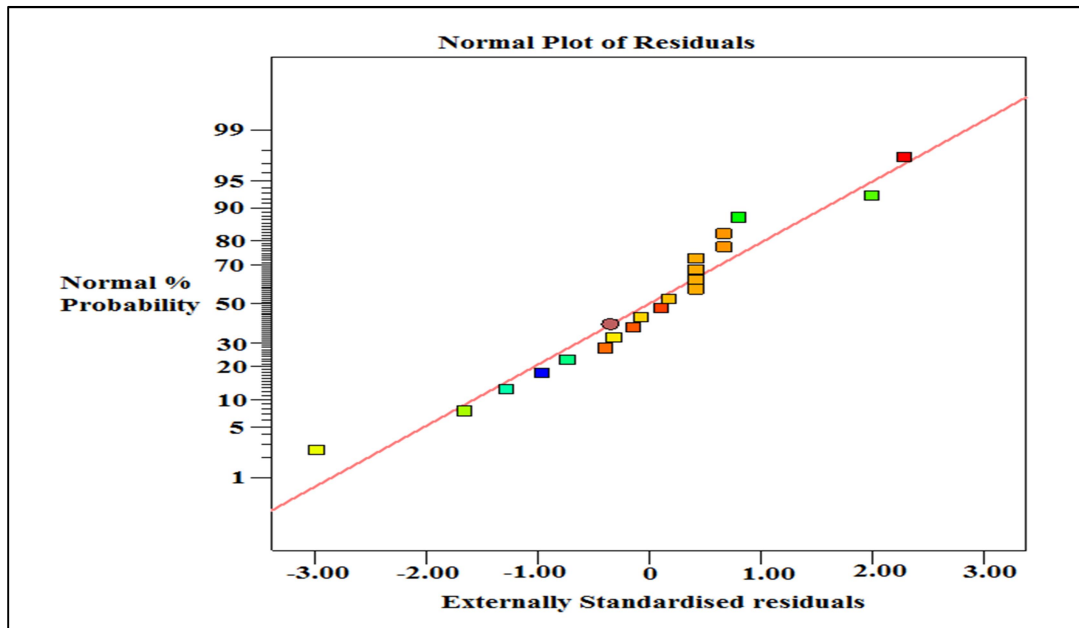


Figure 4.25: Normal Plot of Water Consistency

The normal probability plot of the effect on water consistency residuals shows no particular pattern showing normality of the data in Figure 4.25.

Residual versus predicted

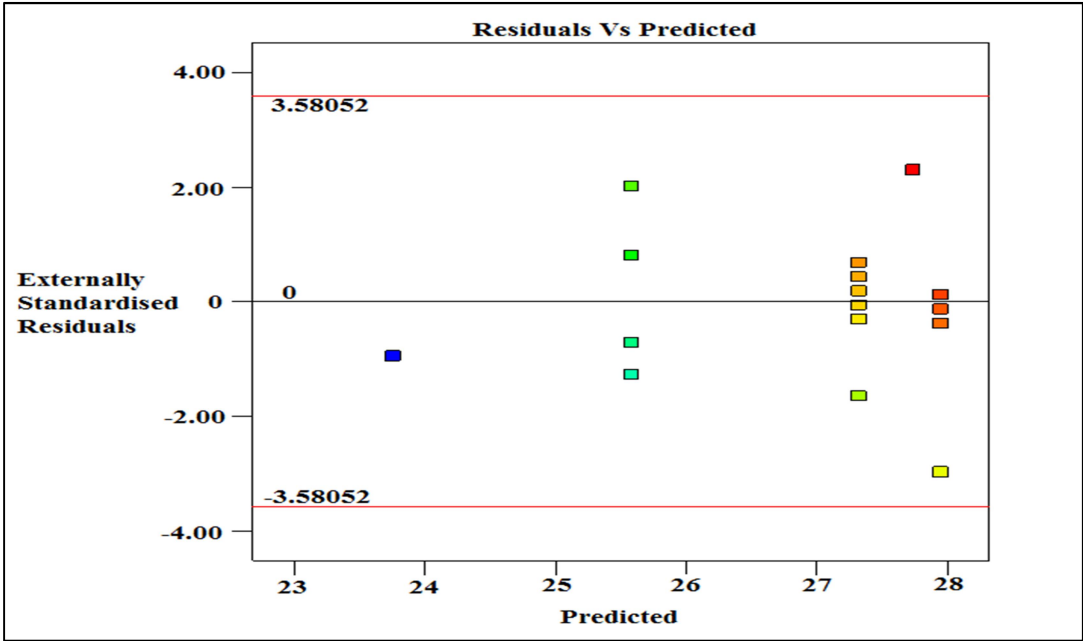


Figure 4.26: A graph of Standard Residuals Vs Predicted of Expansion.

From the graph above standard residuals are randomly distributed around zero with no particular pattern. There are no outliers showing validity of the model. This is determined by no points beyond the border lines around ± 4.0 of externally standardised residuals.

3D Surface Plot

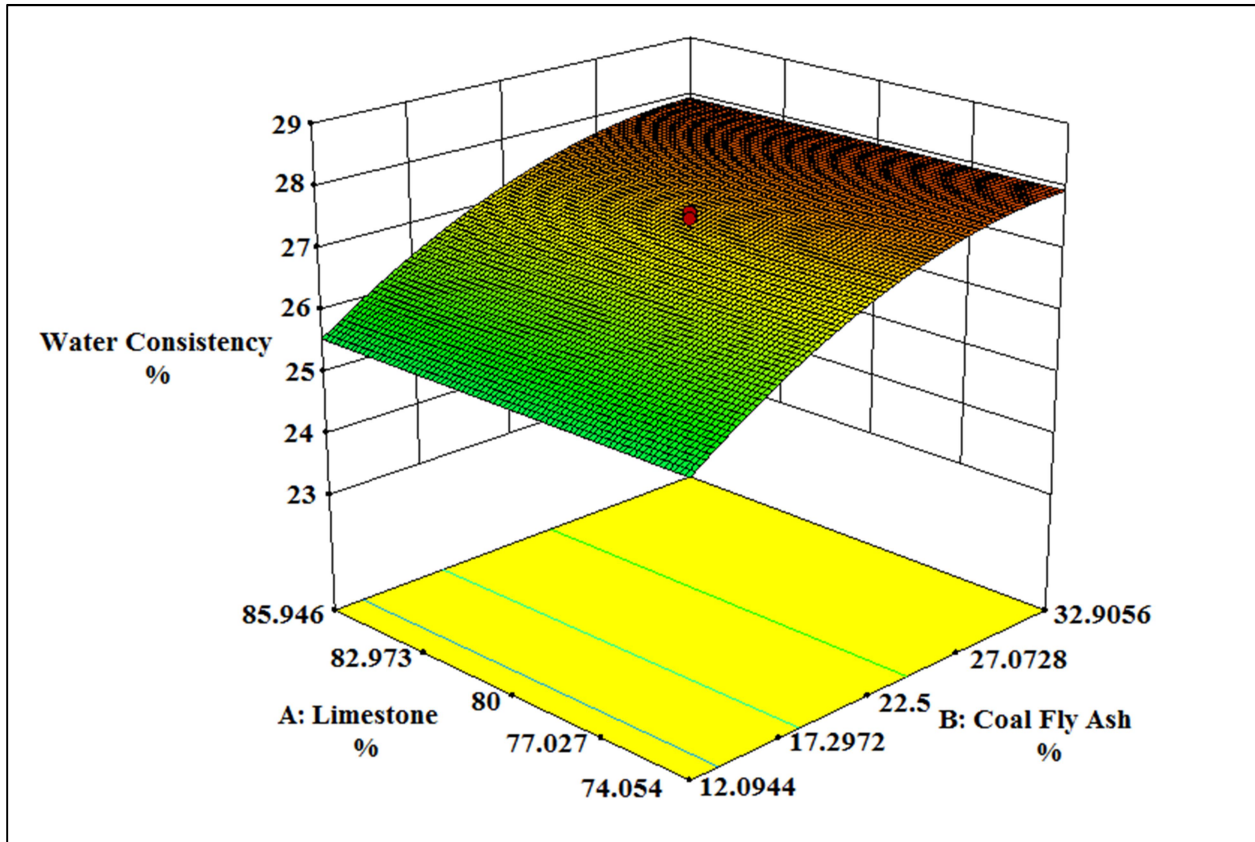


Figure 4.27: 3D Surface plot of the effect of Limestone Vs CFA on Water Consistency.

The plot above showed an increase in water consistency with an increase in CFA, this is due to the fact that water consistency is directly proportional to fines of cement and as we increase the CFA the fines of cement increases [47]. It can also be observed from the plot that an increase in limestone does not affect water consistency.

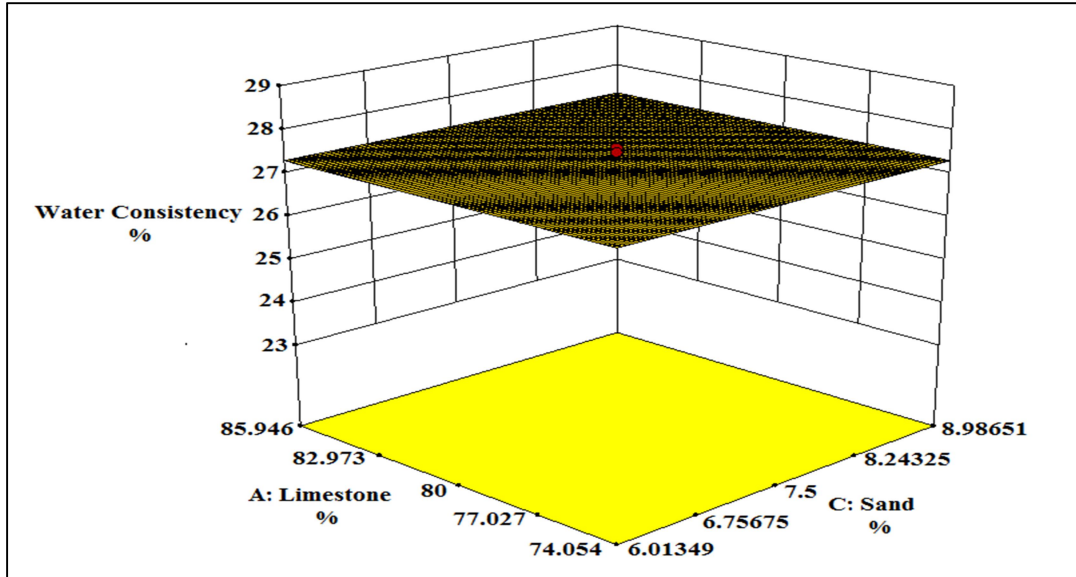


Figure 4.28: 3D Surface plot of the effect of Limestone Vs Sand on Water Consistency.

Figure 4.28 is a 3D surface plot which shows that an increase in both limestone and sand has no significant effect on the water consistency of the cement.

Trend analysis of setting time

From the above results it can be observed that Limestone and sand do not have a significant effect on water consistency as compared to CFA.

4.5 Optimization

From all the parameters that were analyzed in this research it was observed that setting time, expansion and consistency were all affect by different volumes of CFA but they were all in the SAZ and International Standards tolerance range[46].

All the factors had an influence on the strength of the cement, the optimization data that was generated by excel as well as the design expert software is shown in Table 4.13 below.

Table 4.12: Strength Optimization Results

	Limestone (%)	CFA (%)	Sand (%)	Strength (MPa)
2days	76.6408	32.9055	8.9865	40.9431
7days	85.0038	24.4902	8.6528	43.6673
28days	85.3203	20.3016	8.8510	39.3561
48days	84.1962	17.0505	8.9865	39.0587

From the data it observed CFA does play a major role in the early day strength and Limestone plays a major role in the later day strength. It can be deduced from the optimization results and the experimental graphs that if volumes of CFA of about 17.00 – 20.00% are used they will no greater rearrangement during the later days and the early day strength will be around 30 MPa which is greater than the strength produced by OPC of about 14MPa[23]. It was also observed that more volumes of Limestone aid in the later day strength but good strength results are obtained when volumes of about 84.00-85.50% are used.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

CFA was utilized as a raw material in the production of cement. From the research it was observed that CFA plays a major role in all the physical parameters of cement. CFA plays a significant role in the early day strength of cement as it was seen from the optimized results that volumes of CFA of about 32.91% will reach a 2 days' strength of 40.9431MPa.

From the obtained results it was seen that Limestone and Sand play a major role in the later day strength of cement. The research showed that CFA can be used as raw material, and it can be incorporated with sand and Limestone to produce a cement that has greater early day strength and later day strength.

From the optimized data it was seen that CFA volumes of 17.05 to 20.30% will produce cement strength that will be around 30MPa and if it is incorporated with Limestone volumes of 84.00 to 85.00% and Sand volumes of 8.80 to 8.90% the later day strength will be around 39MPa. These strength results are actually greater than the expected strength of OPC according to the ASTM standards[59,29].

CFA chemical analysis showed that it has more aluminium oxide than Kaolin thus it can be used as substitute for kaolin.

5.2 Recommendations

In view of the research findings and conclusion of this research, the following recommendations are made:

- A composition of raw mix design that has 85.32% Limestone; 20.30% CFA and 8.85% Sand will have early day strength (2 days' strength) of above 30MPa and later day strength (28 days' strength) of about 39.3561MPa.
- Also, a composition of raw mix design that has 84.20% Limestone; 17.05% CFA and 8.99% Sand will have early day strength (2 days' strength) of above 30MPa and later day strength (48 days' strength) of about 39.0587MPa.
- CFA percentages above 20.30% will produce early day strength of about 40.9431MPa but will lead to greater conversion and thus a great reduction in the later day strength of the cement, therefore CFA percentages must not be used in the range 17.05 to 20.30%, here good early and later days' strength of the cement will be observed.
- Other experimental designs and different statistical stools must be done to investigate the effect of CFA as a cement raw material.

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APPENDIX A: SPECIFICATIONS

SAZ Specifications EN 197-1(2000) Portland cement (A-M(S) 32.5N)

PARAMETER		SAZ SPECIFICATION
Compressive strength	2day	≥ 12 Mpa
	7day	≥ 16.0 Mpa
	28 day	32.5-52.5 Mpa
Setting Time	initial	≥ 75 mins
	Final	Not Specified
Expansion		≤ 10.0 mm
Sieve Residue		$\leq 15.0\%$
Water Consistency		Not Specified

APPENDIX B: REAGENTS

A summary of material and reagents used in this research

MATERIAL	DESCRIPTION
Standard Sand	Use for standard motor preparation.
Deionized water	Pure water for laboratory use
Coal Fly Ash	Raw Material under study

Clinker	Specimen under study
Cement sample	Specimen under study

APPENDIX C: EQUIPMENT

A summary of the test equipment used in this research

EQUIPMENT	MODEL
XRF	AXIOS-FAST
Bomb Calorimeter	SDAC600
Jolting apparatus	E132N- 1992
Moulding equipment	65-L0010/5
Curing cabinet	Scientec 141 RSA
Fusion machine	FLUXANA-VI0005
Compression machine	TONIK-UTC4231
Weighing balance	ES124-4(max 900)
Vicat equipment	GBT T1346-2001
Pelletizer	YYJ-40 Force spectro
Boiling box	BB 5230B-420
Oven	ML-3-4 9327

Muffle Furnace	BST/MF/1800
Laboratory mill	V-15 mixer 991203

APPENDIX D: CALCULATIONS AND METHODOLOGY

Determination Compressive strength

Sample preparation: Cement, deionized water and standard sand will be mixed thoroughly using a hobart electric mixer mixer and a mixing bowl. The cement mortar will be moulded using standard moulds of 40mm x 40mm x 160mm and clamped on a jolting machine for compaction. The compaction will be repeated both at low speed and at high speed. After compaction, the moulds will be leveled and removed from a jolting table and then placed in a humidity cabinet for 24 hours. The cabinet conditions will be set at 24°C and 95% humidity. The specimens will be de-molded after 24 hours and for each test work, twelve cubes will be produced, that is 3 cubes for each 2-day, 7-day, 28-day and 48-day testing respectively. The above specimens will be cured for 2-day, 7-day, 28-day and 48-day respectively in curing cabinets at 24°C and 90% humidity (standard conditions). After reaching the above ages, the cubes will be tested for and compressive strength.

compressive strength:

- Power supply of the hydraulic compression testing machine will be switched on, machine started and allowed to warm up for 15minutes
- Half of each specimen from the curing cabinet will be divided into two.

- Half of each specimen from the curing cabinet will be placed on the compressive machine.
- Each halve prism will be centred laterally on the platens of the machine within $\pm 0.5\text{mm}$ and longitudinally such that the end face of the prism overhangs the platens or auxiliary plates by 10mm.
- Delivery valve of the compression machine will be turned on and the machine started to compress.
- The load will be smoothly increased over the entire load at a rate of 2400N/S until the specimen fractures, the maximum load reached and recorded as compressive strength
- After the fracture, the delivery valve will be turned off whilst the reflux valve turned on.
- Calculate the mean of the six half prism compression test results. Check if any one value is out by more than 10% from the mean. If any value falls outside the $\pm 10\%$ limit, discard the value that furthest away from the mean and re-calculate the mean. If any of the remaining results is further away than 10% of the new mean, discard the value and repeat the whole test with a fresh sample of the same cement.

Determination of standard consistency

- A weighed cement sample of 500g will be placed in a bowl.
- A measured amount of water will be added slowly into the mixer bowl containing the cement sample in not more than 10seconds, stop watch will be started from the time the first drop of water is added.

- The mixer will be started immediately and run at low speed for 90seconds.
- The machine will be stopped after 90 seconds for 15seconds during which any paste adhering to the bowl outside the mixing zone is returned to the mix with a suitable scraper.
- The machine will be restarted and run at low speed for a further 90seconds (The total mixer running time shall be 3 minutes)
- The paste immediately transferred to the mould, which has previously been placed on a lightly greased plane glass base-plate and filled to excess without undue compaction or vibration. The excess will be removed by a gentle sawing motion with a straight edged implement in such a way as to leave the paste filling the mould and having a smooth upper surface.
- The Vicat apparatus will be calibrated with the plunger attached in advance of the test, by lowering the plunger to rest on the base plate to be used and adjusting the pointer to read zero on the scale.
- The plunger will be raised to the stand-by position.
- The mould and base plate will be transferred to the Vicat apparatus and positioned centrally under the plunger, the plunger lowered gently until it is in contact with the paste
- The moving parts will be quickly released and allow the plunger to penetrate vertically into the centre of the paste.

- The scale will be read when penetration has ceased or 30s after the release of the plunger, whichever is earlier, then reading recorded which indicates the distance between the bottom face of the plunger and the base plate
- The test will be repeated until the distance between plunger and base plate is 6 ± 1 mm.
- The water content of the paste will be recorded to the nearest 0.5% and expressed as a percentage by mass of cement as the water of standard consistence
- Transfer the standard paste to the curing cabinet for setting time test and autoclave expansion [32]

Determination of setting time

From the standard paste prepared in standard consistence procedure:

- The Vicat mould which had been placed on a lightly greased plane glass base-plate and filled (without undue compaction or vibration) to excess with paste of standard consistence will be levelled.
- The mould and base plate will be transferred to the Vicat apparatus and positioned centrally under the needle, the plunger lowered gently until it is in contact with the paste
- The moving parts will be quickly released and allow the needle to penetrate vertically into the centre of the paste.
- The scale will be read when penetration has ceased or 30seconds after the release of the plunger, whichever is earlier, the scale reading recorded, which indicates the distance between the end of the needle and the base-plate together with the time from zero

- At an interval of 10 minutes, the penetration will be repeated with a clean needle.
- The time measured from zero at which the distance between the needle and the base-plate is $4\pm 1\text{mm}$ will be recorded as the initial setting time of the cement.
- The mould is then inverted from the determination of initial setting time on its base plate so that the test for final set is made on the specimen in contact with the base plate. The needle is changed with the needle for final setting and the hole in the final needle is checked if it is open, it is then placed gently onto the surface of the paste, if the centre point an impression and the cutting edge does not, then the final set has been reached, then it is repeated for 3 or more times on other areas of the paste. The time is then recorded close to 15 minutes.

Determination of expansion volume of cement paste

From a cement paste that has passed standard consistency test, the following will be carried out:

- The standard cement paste will be moulded into a Le-chatelier apparatus and covered with a pair of lightly oiled glasses
- The specimen will be stored in humidity cabinet for 24 hours at standard conditions, 24 ± 1 degrees and humidity of 90% and above
- After 24 hours of curing, width of the Le-Chatelier needles with specimen will be measured and recorded.
- The specimen will be heated at boiling temperatures for 3 hours.

- The specimen will be removed from the water bath and the length of the Le-chatelier needles re-measured after boiling. The difference between final and initial measurements after autoclaving will be recorded and results of expansion volume of cement paste then calculated as: Length of needles after boiling – Length of needles before boiling.