PROPERTIES OF CORN COB ASH CONCRETE

BY

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DECLARATION

I hereby declare that this dissertation was written by me and that it is a record of my own research findings. It has neither been taken nor accepted anywhere before, in fulfillment of the award of any degree.

All quotations are indicated and sources of information are specifically acknowledged by means of references

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CERTIFICATION

This dissertation titled: **"PROPERTIES OF CORN COB ASH CONCRETE"** by Engr. Aimola Taiwo Christopher meets the regulations governing the award of Doctor of Philosophy in Civil Engineering of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation

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ABSTRACT

This thesis studied the behavior Corn Cob Ash (CCA) concrete. The study also investigated the effect of Corn Cob Ash on cement and as a partial replacement for cement. The behavior of Corn Cob Ash concrete in aggressive chemical media was then investigated. Chemical analysis of the CCA to determine the elemental oxide composition revealed that it was pozzolanic. CCA is classified in class F using ASTM C618. The effect of using CCA on water/cement ratio of the standard consistency paste as well as initial and final setting times of cement paste revealed that both initial and final setting times increased with increase in the CCA content. Increased substitution of cement with CCA did not affect the soundness of cement adversely. The strength properties of Corn Cob (CCA) concrete were studied using up to 50% CCA as replacement for cement in concrete. The strength of CCA concrete increased with curing period but decreased with increase in CCA content. Increased replacement of cement with CCA reduced the density of concrete and there was a decrease in weight as curing age of cube increased. Durability study of CCA concrete carried out with specimen immersed in 5% and 10% solutions of Acetic acid, Sulphuric acid and Sodium sulphate solutions revealed that in compressive strength increased as age of curing increased in acidic solutions. Loss of weight of CCA concrete with age in chemical solution increases with the increasing acid concentration. For each set of specimen, it was observed that as the acid concentration increases, the extent of surface deterioration also increased.

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CHAPTER ONE

INTRODUCTION

1.1 Background of study

The search for alternative binder or cement replacement materials led to the discovery of the potentials of using industrial by-products and agricultural wastes as cementitious materials. If these fillers have pozzolanic properties, they impart advantages to the resulting concrete and also enable larger quantities of cement replacement to be achieved (Biricik et al., 1999)

Corn cob is an agricultural waste product obtained from maize or corn. According to Food and Agriculture Organization (FAO) data, 589 (million tons) of maize were produced worldwide in the year 2000. The United States was the largest maize producer having 43%, of world production. Africa produced 7% of the world's maize. Nigeria was the second largest producer of maize in Africa in the year 2001 with 4.62 million ton with South Africa having the highest production of 8.04 million ton that year.

The incorporation of pozzolanic waste ash in concrete can significantly enhance its basic properties in both the fresh and hardened states (Ahmed 1993. Chandra 1997). These materials greatly improve the durability of concrete. The utilization of by-products as the partial replacement of cement has important economic, environmental and technical benefits such as the reduced amount of waste materials, cleaner environment, reduced energy requirement, durable service performance during service life and cost effective structures.

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1.2 Statement of research problem

The use of waste materials for partial replacement of cement provides for greater economic and environmental benefits Nazir *et al* (2009). A considerable amount of work has been reported in the literature on how to use agricultural waste products as supplementary cementitious materials Mehta (2000). Because of their cementitious or pozzolanic properties these can serve as partial cement replacement. Ideally, the development of such materials serves three separate purposes simultaneously.

On the one hand, waste by-products have an inherent negative value, as they require disposal, typically in landfills, subject to tipping fees that can be substantial. When used in concrete, the material's value increases considerably. The increase in value is referred to as "beneficiation". As this supplementary cementitious material (SCM) replaces a certain fraction of the cement, its market value may approach that of cement. The use of SCM reduces the cost of construction and could make it more affordable to poor masses.

A second benefit is the reduction of environmental costs of cement production in terms of energy use, depletion of natural resources, and air pollution. Also, the tangible as well as intangible costs associated with landfilling the original waste materials are eliminated.

Finally, such materials may offer intriguing additional benefits. Most concrete mixes can be engineered such that the SCM will give the mix certain properties (mechanical strength, workability, or durability) which it would not have without it.
The task however is developing a mix design, to combine these three different goals in an optimal way such that the economic benefits become transparent.

1.3 Aim and objectives of study

The aim of the study is to determine the properties Corn Cub Ash as a pozzolana in concrete with the following objectives;

1) Study the behaviour and physico – mechanical properties of corn cob ash cementitious mixtures.
2) Determine the strength properties of concrete modified with corn cob ash as partial replacement for cement
3) To study the deterioration mechanism and the influence of various chemical media on the physico – mechanical properties of Corn Cob Ash modified concrete.
4) Using Statistical methods generate models that describes the physico – mechanical behavior of Corn Cob Ash modified concrete

1.4 Justification for the study

Corn Cob Ash are a residue produced in significant quantities on a global basis. While they are utilized in some regions, in others they are a waste causing pollution and problems with disposal. It is well known that blending cement with ash or other supplementary cementing materials improves the engineering properties of hardened concrete and the rheological properties of the fresh concrete. These improvements are generally attributed to both the physical and chemical effects. When combusted, Corn Cob Ash is pozzolanic and suitable for use in lime-pozzolana mixes and Portland cement replacement. Pozzolans are used for both their cost reducing and performance enhancing properties. The proper engineered use of this material can greatly enhance workability, setting times, density, porosity, durability and strength gain characteristics.

A second benefit is the reduction of environmental costs of cement production in terms of energy use, depletion of natural resources, and air pollution. Also, the tangible as well as intangible costs associated with landfilling the original waste materials are eliminated.

1.5 Outcome of Study

Chemical analysis of the ash showed that the ash contained essentially of reactive silicon dioxide (SiO2), (65.1 %), and is pozzolanic and satisfies the requirements of ASTM class N and F. The effect of using CCA as a partial replacement for cement on the standard consistency paste as well as initial and final setting times of cement paste shows that both initial and final setting times increase with increasing CCA content. Increased CCA content did not affect the soundness of cement adversely.

The strength properties of Corn Cob (CCA) concrete showed that the strength of CCA concrete increased with curing period but decreased with increasing CCA content. Increased substitution of cement with CCA reduced the density of concrete. A durability study of CCA concrete in 5% and 10% solutions of Acetic acid, Sulphuric acid and Sodium sulphate solutions revealed that there was an increase in compressive strength in cube specimens as age of curing increased in acidic solutions. For each set of specimen, it was observed that as the acid concentration increases, the extent of surface deterioration also increases.

CHAPTER TWO

LITERATURE REVIEW

2.0 Cementitious Reactions of Portland Cement

Calcium combination with silica, aluminum and iron oxide are essentially crystalline compounds cement is made of. These compounds are essentially regarded as the major constituent's portland cement. The actual quantities of the various compounds vary considerably from cement to cement, and in practice different types of cement are obtained by suitably proportioning these materials. Along with the major compounds there exist minor compounds such as SO_3, MgO, K_2O, Na_2O, which normally amount to not more than a few percent by weight of the cement.

The compounds of the portland cement clinker are anhydrous, but when water is added they begin to ionize, and the ionic species form hydrated products of low solubility that precipitate out of the solution. The main product of the hydration of silicates mineral is calcium hydrate silicate (C-H-S) of colloidal dimension, that at an early age, under scanning electron microscope, usually shows up as an aggregation of very fine grains partly inter-grown together.

The structure of C-H-S is not constant in space and time. It adopts a variety of morphologies, some based on thin sheets to give fibrous or honey comb structure at an early age, while others have a more complex structure Reinhardt (1995). It is highly cementitious and constitutes about 60 to 65 percent of the total solids of the hydrated cement. The other product of the hydration of the silicate minerals is about 20 percent calcium hydroxide (CH) which usually occurs as large hexagonal crystals, and contributes little to the cementitious properties of the system. Also, being relatively soluble and alkaline than the other products of hydration, it is easily subjected to attack

by water and other acidic solution. This reduces the durability of portland cement systems in such environments Mehta (1983).

2.1 History of Pozzolan

It is stated in the literature that there are 1282 volcanoes in the world considered to have been active in the past ten thousand years, and only 3 of these volcanoes deposited high quality natural pozzolan. The first one is Santorini Volcano, Greece, which erupted during 1600 BC - 1500 BC. Mt. Vesuvius, Italy, is the second volcano which erupted in AD 79. Pozzolan was named after the town of Pozzoli where it was deposited. The third, Mt. Pagan, is the only one which has erupted in modern times. Scientists have proven that the ancient Greeks began to use natural pozzolan-lime mixtures to build water-storage tanks some time between 700 BC and 600 BC. This technique was then passed on to the Romans about 150 BC. According to Roman engineer Vitruvius Pollio who lived in the first century BC: "The cements made by the Greeks and the Romans were of superior durability, because neither waves could break, nor water dissolve the concrete." Many great ancient structures, such as the Coliseum, the Pantheon, the Bath of Caracalla, as well as other structures that are still standing in Italy, Greece, France, Spain and the islands in the Mediterranean Sea, were built with natural pozzolan-lime mixtures. Many of them have lasted more than two thousand years. After the invention of Portland cement, natural pozzolan was used as a concrete strengthening additive to improve characteristics, such as durability, compressive strength, chemical resistance, hydration heat, permeability, etc. In Europe and the USA, there have been numerous high rise buildings, highways, dams, bridges, harbors, canals, aqueducts and sewer systems built with natural pozzolan-cement mixtures.

2.1.1 Pozzolanas and lime-pozzolanas

In general, pozzolanas are classified into two groups: natural and artificial. A pozzolana is a material which, on its own, is not cementitious but, with the addition of lime, reacts to form a material which sets and hardens. Thus, for the purpose of construction, a pozzolana is not an end in itself but, rather, a means of achieving the ultimate product - lime-pozzolana. Lime-pozzolana is a low-strength binder used in the same manner as lime, to prepare mixtures for mortars, plasters and building blocks and for soil stabilization. Normally, a mixture of one part of lime to two parts of pozzolana is adequate for lime-pozzolana binders, and, even if a ratio of 1:1 is applied, considerable savings of about 50 per cent of the available supply of lime is achieved. In this way, where pozzolana is obtained at a lower cost than lime, lime-pozzolana becomes an attractive material for low-cost construction.

2.1.2 Natural pozzolanas

Natural pozzolanas are basically of volcanic origin and are usually found in areas which have experienced volcanic activities. For example, in Africa, natural pozzolana deposits can be found in six countries -Burundi, Cameroon, Caper Verde, Ethiopia, Rwanda and the United Republic of Tanzania. Pozzolanas of this type occur either in a pulverized state or in the form of compact layers, and this, in turn, determines the production process which the pozzolana has to undergo before being mixed with lime to produce a binder.

Where volcanic tuff occurs as a naturally fine-grained material, it requires no preparation apart from ensuring that it is sufficiently dry prior to mixing with lime. Sun-drying is feasible, even though a small-scale, locally fabricated kiln can be used for this purpose. For example, the Arusha-Moshi area of the northern part of the United

Republic of Tanzania is volcanic, and large deposits of fine-grained pozzolanas are widely available. These deposits which require no grinding after quarrying can be mixed with lime to prepare mortars, plasters and building blocks.

Where the natural pozzolana occurs in a coarse-grained form, it is desirable to dry the material, either in the sun or a kiln, and, thereafter, grind it in a ball-mill to the desired fineness, ready for mixing with lime. In some instances, the grinding of coarse-grained pozzolanas is restricted to the preparation of mortars and plasters, while the preparation of blocks is feasible without any grinding. For instance, in Lembang, Indonesia, unground coarse-grained pozzolana is mixed with 20 per cent lime and sufficient quantities of water to produce solid blocks for building construction.

2.1.3 Artificial pozzolanas

Unlike natural pozzolanas, artificial pozzolanas are obtained only after the basic materials undergo some basic production processes. The raw materials from which artificial pozzolanas are obtained are extensive in scope, covering materials of geological origin and agricultural and industrial residues Ahmed (1993). However, the most common raw materials used for production of artificial pozzolanas are as follows:

(a) Clay products: Suitable clay deposits can be quarried, fired and ground into fine powder in a ball-mill, for use as a pozzolana. Basically, most soil groups containing the common clay minerals can be used for this purpose, but plastic clays, such as those used for pottery, are the most likely to produce good pozzolanas. The firing of the clay should be under controlled temperatures, and a locally fabricated kiln or incinerator can be used for this purpose. The desired temperature for firing is around 600°C. As an alternative to firing raw clays, pozzolanas can be produced by grinding bricks or tiles

obtained as residual products in the production of fired-clay bricks and tiles. Here, the only equipment required is a ball-mill or a hammer-mill to grind the material. Sometimes, the pozzolana and the lime are mixed and ground together in the ball-mill.

(b) Rice-husk-ash: Rice-husk is the residual product from milling rice. It often has no commercial value but, rather, poses a problem of disposal. The ash which results from burning rice husk is a pozzolana which reacts with lime and water to produce a binder suitable for low-strength masonry application. Normally, about 20 per cent of the volume of rice husk results in ash, and, because rice is grown in several countries, rice-husk-ash is potentially an important cementitious material. In Africa alone, there are about 40 countries where rice is grown, and, even though the quantity of output is not high enough in all the countries to justify commercial-scale production of rice-husk-ash, the potential that exists for promoting the material is encouraging. As a pozzolana, rice-husk-ash is produced under controlled temperatures of about 600°C in a kiln or incinerator. The incinerator for burning rice-husk can be locally fabricated, and, in countries where production has been commercialized, the scale of production if often as small as 1 ton per day. Apart from the incinerator, which can be locally built in bricks, the main capital item required for rice-husk-ash pozzolana manufacture is a ball-mill to grind the ash or ash and lime into a homogenous fine mix. In some countries, the ball-mill may have to be imported but, in a country such as India, it is readily available on the market.

(c) Fly-ash: Fly-ash is the residual product obtained when coal is fired and, thus, occurs as a waste product from coal-fired power stations. It is desirable for the fly-ash to be in a dry state prior to use. Often, fly-lash occurs in a coarse form and will have to be pulverized before mixing with lime to produce a binder, so that the main capital item

required in preparing fly-ash pozzolanas is a ball-mill for pulverizing the ash to the desired fineness.

2.1.4 Blended cements

Blended cements are produced by mixing ordinary Portland cement with a "low-cost" cementitious material, notably, blast-furnace slag, lime or any of the popularly adopted pozzolanas. The principle behind blended cements is to obtain a binder which is nearly equal in strength to Portland cement but, at the same time, cheap in cost. Examples of blended cements are Portland-pozzolana, Portland-slag or Portland-lime pozzolana. There are cases where blended cements have been produced by replacing about 25 per cent of the volume of Portland cement with a pozzolana, and the resulting binder is recorded to have satisfied the same 28-day strength test as for normal Portland cement. Blended cements have an advantage over Portland cement in terms of workability and water resistance Antiohos *et al*.(2005).

The production of blended cements is in two stages. First, the production of pozzolana and, secondly, the inter-grinding of pozzolana or lime with Portland cement. The use of rice-husk-ash to produce blended cements has been gaining popularity over other types of pozzolana, and some demonstrations have indicated that up to 50 per cent of Portland cement can be replaced by rice-husk-ash, with only a marginal reduction in the strength of the resulting binder compared with normal strengths of Portland cement. The cost implications of blended cements could be very encouraging, as demonstrated in Rwanda where pozzolana-lime-cement is estimated to be 50 per cent the cost of Portland cement.

Unlike lime-pozzolana, the production technology for blended cements is relatively intricate. First, the production presupposes the availability of Portland cement;

secondly, it is desirable to produce a finely ground pozzolana for the purpose of blending with the cement. However, the part of the operation which requires careful control is the inter-grinding of the pozzolana or lime with the cement into a homogenous mixture, of uniform degree of fineness. For these reasons, blended cement manufacture is, in general, a capital-intensive process even though the capital-intensity per ton of output is still far less than Portland cement.

2.2 Pozzolana

Pozzolanas have been used to improve properties of cement mortar and concrete. Pozzolanas, by their diverse and varied nature, tend to have widely varying characteristics. The chemical composition of pozzolanas varies considerably, depending on the source and the preparation technique. Generally, a pozzolana will contain silica, alumina, iron oxide and a variety of oxides and alkalis, each in varying degrees.

Pozzolanic materials do not harden in themselves when mixed with water but, when finely ground and in the presence of water, they react at normal ambient temperature with dissolved calcium hydroxide ($Ca(OH)_2$) to form strength-developing calcium silicate and calcium aluminate compounds. These compounds are similar to those which are formed in the hardening of hydraulic materials. Pozzolanas consist essentially of reactive silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3). The remainder contains iron oxide (Fe_2O_3) and other oxides. The proportion of reactive calcium oxide for hardening is negligible. The reactive silicon dioxide content shall be not less than 25% by mass BS 197 part 1(2000).

The American Society for Testing and Materials (ASTM) is probably the most widely recognized and used national standards-setting organization in the United States for engineering-related materials and testing. The ASTM C618 (1992) specification (see

table 1 below) is the most widely used because it covers the use of fly ash as a pozzolan or mineral admixture in concrete. The three classes of pozzolans are Class N, Class F, and Class C. Class N is raw or calcined natural pozzolan such as some diatomaceous earths, opaline cherts, shales; tuffs, volcanic ashes, and pumicites; and calcined clays and shales. Class F is pozzolanic fly ash normally produced from burning anthracite or bituminous coal. Class C is pozzolanic and cementitious fly ash normally produced from burning lignite or sub-bituminous coal.

The inclusion of pozzolana as a partial replacement to cement improves significantly the characteristics both to concrete and cement paste. Apart from fly ash, agricultural wastes such as rice husk ash, pea nut shell ash and fiber shell ash have been used as cement substitutes (Bentru et al, 1986; Abu 1990; Mehta1992; Anwar,1996) Among them, rice husk ash has been distinguished as an active pozzolana in the production of high performance concrete and cement products.

Udoeyo *et al*.(2003) investigated an innovative use of maize-cob ash (MCA) as a filler in concrete. MCA in the range of 0-30% was used as a partial replacement for ordinary portland cement in a concrete of mix ratio 1:2:4:0.6 (cement: sand: coarse aggregate: water-cement ratio). Fresh concrete properties, compressive, split tensile strengths, and modulus of rupture were measured for concrete mixtures with MCA within the investigated replacement levels. The results showed that the setting times of MCA concrete increased with higher ash content, while the compressive, split tensile strengths and modulus of rupture showed a reverse trend. It was further observed that almost all of the studied specimens attained over 70% of their 28-day strength at seven-day curing (Nimityongskul et al, 1993).

Combination of pozzolanic materials having cementitious properties also been studied Chai et al (2003). In their paper, they proposed a new cementitious material from a mixture of calcium carbide residue and rice husk ash. Calcium carbide residue and rice husk ash consist mainly of $Ca(OH)_2$ and SiO_2, respectively. The cementing property was identified as a pozzolanic reaction between the two materials without portland cement in the mixture.

Table 2.1: Summary - ASTM C618 Classification of Pozzolan

Chemical			F	C	N
	$SiO_2 – Al_2O_3 – Fe_2O_3$	min %	70	50	70
	SiO_2	max %	5	5	
	Moisture Content	max %	3	3	3
	Loss of ignition	max %	4	6	10
Optional Chemical					
	Available Alkalis	max %	1.5	1.5	1.5
Physical					
	Fineness + 325 Mesh	max %	34	34	34
	Strength Activity/Cem.	min %	75	75	75
	Water Requirement	max %	105	105	15
	Autocave Expansion	max %	0.5	0.8	0.8
	Uniformity Requirements				
	Density Max. Var.	max %	5	5	5
	Fineness Foits Var.	max %	5	5	5
Optional Physical					
	Multiple factor		225	-	-
	In Drying Shrinkage	max %	0.03	0.03	0.03
	Uniformity Requirements				
	A.E. Admixture Demand	max %	20	20	20
	Control of AS				
	Expansion % of raw alkali cement	max %	100	100	100
	Sulphate Resistance				
	Moderate exposure 6 months	max %	0.10	0.10	0.10
	High exposure 6 months	max %	0.05	0.05	0.05

Various research workers in the recent past had look into the utilization of agricultural wastes that are known to be pozzolanas to partially substitute cement that is the major component of concrete. The use of Ordinary Portland Cement (OPC) and Rice Husk Ash (RHA) concrete in minimizing thermally induced expansion cracks has been identified by Neville (2000). This is because the OPC/RHA paste hydrates slowly and therefore evolved low heat making them suitable for use in concrete in the tropics. Okpala *et al* (1987) recommended the use of 40% partial replacement of the OPC with RHA. Mbachu *et al*. (1998) examined the influence of coarse aggregate on the drying shrinkage and elastic moduli of concrete with OPC partially replaced with RHA. Results showed that OPC/RHA concrete cast with quarry granite as coarse aggregate exhibited the least drying shrinkage over time and also gave the highest values of elastic moduli when compared with river gravel. In a related work on Groundnut Shell Ash, Yusuf (2001) reported that 30% partial replacement of cement with Groundnut ash gave better results in the strength of the composite concrete when compared with the control Alabadan *et al* (2006).

2.3 Advantages of Pozzolan:

The modern use of pozzolans as a cement replacing or enhancing admixture in concrete began many decades ago, and is not new to the construction industry. However, a trend in the past decade towards greater usage is now redefining acceptable practice. Often restricted by building codes to small fractions of the cementitious material in a concrete mix, pozzolans have held a relatively minor role in the concrete industry, especially in the USA and North America. Three trends are now active that are changing that minor role to a much bigger one, these trends are discussed below.

2.3.1 Economy

Portland cement, the primary "glue" for structural concrete, is expensive and unaffordable for a large portion of the world's population. Some pozzolans, for various reasons, are also expensive, but the most abundant and widely available, fly ash, is not, and typically costs about half as much by weight as cement. Blended cements that replace up to 60% of the Portland cement with fly ash are successfully used in structural applications. Since Portland cement is typically the most expensive constituent of concrete, the implication is greatly improved concrete affordability.

2.3.2 Durability

A wide variety of environmental circumstances are deleterious to concrete, such as reactive aggregate, high sulfate soils, freeze-thaw conditions, exposure to salt water, deicing chemicals, and acids. Typically, these problems have been partially overcome by utilizing special cements, increasing strength, and/or minimizing water/cement ratios. But there now exists an overwhelming body of laboratory research and field experience showing that the careful use of pozzolans is useful in countering all of these problems (and others); pozzolan is not just a "filler", as many engineers think, but a strength and performance-improving additive. In general terms, the siliceous pozzolans react with the(non-cementitious) calcium hydroxide in hydrated cement paste to produce (highly cementitious) calcium silicate hydrates that yield higher strength and dramatically reduced permeability.

2.3.3 Environment

Portland cement requires a significant amount of heat in its manufacture, making it expensive not just to the consumer, but to the atmosphere as well. As mentioned

earlier, for every ton of cement produced, roughly one ton of carbon dioxide (greenhouse gas) is released by the burning fuel, and an additional one ton is released in the chemical reaction that changes the raw material to clinker, making the production of cement responsible for more than 8% of all the greenhouse gases released by human activity. The high-volume use of pozzolans such as fly ash are not just an effective use of "waste" material and an economic savings, but makes possible a noticeable reduction in greenhouse gas buildup. From another perspective, high volume pozzolan usage in blended cements is a way for the cement industry to supply the ever-growing world market without having to build new production facilities. Some pozzolans are manufactured to augment concrete mixes in a specific way, others are ground from fired clay soils (such as the surkhi of India, made by grinding fired clay bricks) and others are volcanic ash such as occurs on Pagan, or diatomaceous soils mined directly from the earth (Feldman *et al*, 1990).

2.3.4 Application in Concrete

Most of the concretes produced today are a multi-component product containing one or more admixtures in addition to the four basic components: cement, water, fine aggregate and coarse aggregate. For every component, one usually has several choices that could influence the cost of the end product and its behavior in service. Among the constituent components, however, cement or cementitious materials as a whole play a vital role in producing strong and durable concrete. For many purposes a pozzolan has been regarded as a substitute for a proportion of cement in a concrete. Incorporation of this pozzolanic material involving replacement of a part of the Portland cement with excess weight of fly ash, replacing also part of the aggregate would to creation a more economical concrete Samarin et al. (1983). The contribution of pozzolana material in

concrete towards improvement of concrete durability has also been highlighted Mehta (1988) and Hoff (1992) who reported that the incorporation of pozzolanic materials such as fly ash, silica flume, and natural pozzolans in concrete contribute to the formation of a denser binder which inhibits the migration of the sea water into concrete. Other researcher (Abdul Awal and

Hussin, (1996) proved that adding POFA for production of concrete would be able to increase the resistance of concrete towards sulphate and acid attack. The role of pozzolan towards improving the properties of concrete has become significant to the extent whereby there are researcher such as Dunstan (1986) who stated that fly ash should be considered to be the fourth ingredient in concrete, that is in addition to the aggregate, cement and water, and not as a replacement of the cement. Conclusively, whatever is the mode of application; all the methods can result in a significant improvement and optimization of certain properties of both fresh and hardened concrete (Salihuddin *et al*, 1993).

2.3.5 Concrete Durability and Strength

Durability and strength are not synonymous when talking about concrete. Durability is the ability to maintain integrity and strength over time. Strength is only a measure of the ability to sustain loads at a given point in time. Two concrete mixes with equal cylinder breaks of 30N/mm^2 at 28 days can vary widely in their permeability, resistance to chemical attack, resistance to cracking and general deterioration over time, all of which are important to durability. Cement normally gains the great majority of its strength within 28 days, thus the reasoning behind specifications normally requiring determination of 28-day strengths as a standard. As lime from cement hydration becomes available (cements tend to vary widely in their reactivity), it reacts with

pozzolana. Typically, concrete made with pozzolana will be slightly lower in strength than straight cement concrete up to 28 days, equal strength at 28 days, and substantially higher strength within a year's time. Conversely, in straight cement concrete, this lime would remain intact and over time it would be susceptible to the effects of weathering and loss of strength and durability.

The paste is the key to durable and strong concrete, assuming average quality aggregates are used. At full hydration, concrete made with typical cements produces approximately 0.11 kg of non-durable lime per 0.45 kg of cement in the mix. Pozzolana chemically reacts with this lime to create more CSH, the same "glue" produced by the hydration of cement and water, thereby closing off the capillaries that allow the movement of moisture through the concrete. The result is concrete that is less permeable, as witnessed by the reduction in efflorescence.

When it comes to concrete durability, engineers should not rely solely on specifying a minimum compressive strength, maximum water-cement ratio, minimum cementitious content and air entrainment. There are better ways to quantify durability. Low permeability and shrinkage are two performance characteristics of concrete that can prolong the service life of a structure that is subjected to severe exposure conditions.

For durability provisions, the ACI 318 Building Code generally relies on the water / cement ratio to reduce the permeation of water or chemical salts into the concrete that impacts its durability and service life. However, along with the w/c, the code requires a concomitant specified strength level, recognizing that it is difficult to accurately verify the w/c and that the specified strength (which can be more reliably tested) should be reasonably consistent with the w/c required for durability. It should be stated that strength should not be used as a surrogate test to assure durable concrete. It is

true that a higher strength concrete will provide more resistance to cracking due to durability mechanisms and will generally have a lower w/c to beneficially impact permeability. However, it should be ensured that the composition of the mixture is also optimized to resist the relevant exposure conditions that impact concrete's durability. This means appropriate cementitious materials for sulfate resistance, air void system for freezing and thawing and scaling resistance, adequate protection to prevent corrosion either from carbonation, chloride ingress or depth of cover, a low paste content to minimize drying shrinkage and thermal cracking, and the appropriate combination of aggregates and cementitious materials to minimize the potential for expansive cracking related to alkali silica reactions Binici (2006).

2.3.6 Concrete Workability

Pozzolana produces more cementitious paste. It has a lower unit weight, which means that on a Kg for kg basis, pozzolana contributes roughly 30% more volume of cementitious material per kg versus cement. The greater the percentage of pozzolana "ball bearings" in the paste, the better lubricated the aggregates are and the better concrete flows. Pozzolana also reduces the amount of water needed to produce a given slump. The spherical shape of pozzolana particles and its dispersive ability provide water-reducing characteristics similar to a water reducing admixture. Typically, water demand of a concrete mix with fly ash is reduced by 2% to 10%, depending on a number of factors including the amount used and class of pozzolana. Pozzolana reduces the amount of sand needed in the mix to produce workability. Because pozzolana creates more paste, and by its shape and dispersive action makes the paste more "slippery", the amount of sand proportioned into the mix can be reduced. Since sand has a much greater surface area than larger aggregates and therefore requires more paste,

reducing the sand means the paste available can more efficiently coat the surface area of the aggregates that are left.

2.3.7 Concrete Permeability

An extremely important aspect of the durability of concrete is its permeability. Pozzolan concrete is less permeable because pozzolans reduces the amount of water needed to produce a given slump, and through pozzolanic activity, creates more durable CSH as it fills capillaries, and bleed water channels occupied by water-soluble lime (calcium hydroxide).

Pozzolans improves corrosion protection. By decreasing concrete permeability, pozzolans can reduce the rate of ingress of water, corrosive chemicals and oxygen, thus protecting steel reinforcement from corrosion and its subsequent expansive result. Pozzolana also increases sulfate resistance and reduces alkali-silica reactivity. While both improve the permeability and general durability of concrete, the chemistry of Class F pozzolans has proven to be more effective in mitigating sulfate and alkali-silica expansion and deterioration in concrete. Some Class C pozzolans have been used to mitigate these reactions, but must be used at higher rates of cement replacement.

Pozzolans concrete can reduce sulfate attack in two additional ways:

(1) Pozzolans reduces calcium hydroxide, which combines with sulfates to produce gypsum. Gypsum is a material that has greater volume than the calcium hydroxide and sulfates that combine to form it, causing damaging expansion.

(2) Aluminates in the cement also combine with sulfates to form expansive compounds. By replacing cement, the amount of available aluminates is reduced, thereby lowering the potential for this type of expansive reaction.

In reducing alkali-silica reactivity, pozzolans has the ability to react with the alkali hydroxides in portland cement paste, making them unavailable for reaction with reactive silica in certain aggregates. Certain studies suggest that greater than 30% replacement with pozzolan for cement has a dramatic effect in combating this expansive reaction.

2.3.8 Hydration in Concrete

The hydration of cement is an exothermic reaction. Heat is generated very quickly, causing the concrete temperature to rise and accelerating the setting time and strength gain of the concrete. For most concrete installations, the heat generation is not detrimental to its long-term strength and durability. However, many applications exist where the rapid heat gain of cement increases the chances of thermal cracking, leading to reduced concrete strength and durability. In these applications, replacing large percentages of cement with pozzolana (Pozzolana generates only 15 to 35 percent as much heat as compared to cement at early ages) can reduce the damaging effects of thermal cracking.

2.3.9 Pozzolan Cement

Pozzolanic concretes need an optimum content of pozzolan to attain the best performances. The amount of pozzolan material used varies depending on the desired properties to be achieved such as better durability or other aspects. Time is also another controlling factor in selecting the amount of pozzolan to be integrated in the mix. For example, after 3 days of curing, a 15 percent replacement of a Portland cement for 15 percent fly ash gave in the majority of cases a higher compressive strength than that of the control cement. However, too much of pozzolan content in concrete mix would give

negative effect towards the concrete strength development Massazza (1993). This is because utilization of too much pozzolanic material as partial cement would lead to reduction in the amount of cement thus reducing the amount of calcium hydroxide produced from hydration process. As a result, the early strength of concrete would be very low and the belated strength development which depends on the pozzolanic reaction could not increase the strength much since not all pozzolana material could react with the free lime.

2.3.10 Particle Size Distribution

It is a well-known fact that the increase in the fineness of pozzolan material would lead to significant increase in strength. The extremely fine particles in concrete act as lubricant in the concrete mix and permits a reduction in water content, thereby, increasing strength. Additionally, the fly ash spheres with their multi-sized spherical morphology promote a high packing density of plastic concrete. The influence of ash fineness towards strength development of concrete has been investigated by many researchers. Mehta (1992) reported that RHA samples with large surface area and small crystal size reacted faster with lime, whereas ashes with low surface area and containing silica in crystalline form showed low reactivity. Similarly, Mahmud et al. (1989) who conducted research on the effect of RHA fineness upon strength of concrete also discovers that fineness of ash used tend to influence the strength exhibited by concrete. Not only that, the fineness of pozzolanic ash also tends to affect both the fresh and hardened state properties of concrete Abdul Awal (1998). Generally, the ash used as pozzolanic material need to be produced in a finer size so that it can function effectively in increasing the strength of concrete.

2.4 Testing methods for pozzolanas

Pozzolanas, by their diverse and varied nature, tend to have widely varying characteristics. The chemical composition of pozzolanas varies considerably, depending on the source and the preparation technique. Generally, a pozzolana will contain silica, alumina, iron oxide and a variety of oxides and alkalis, each in varying degrees. This presents problems for small-scale manufacturers wishing to use pozzolanas in a lime or OPC - pozzolana mix. Where there are no laboratory facilities available for testing the raw materials, then it is difficult to maintain standards and produce a consistent product. It is also generally agreed that although the chemical content of a raw material will determine whether or not it is pozzolanic and will react when mixed with lime or OPC, the degree of reaction and subsequent strength of the hydrated mixture cannot be accurately deduced from just the chemical composition (except for a small number of known pozzolanas .

In most cases no direct correlation can be found between chemical content and reactivity. Other characteristics of the pozzolana also affect its reactivity, such as fineness and crystalline structure. It is also argued that because pozzolanas are used for a variety of different applications, such as in mortars, concretes, block manufacture, etc., and mixed with a variety of other materials such as lime, OPC, sand, etc., (which can also radically affect the reaction of the pozzolana), then perhaps it is better to develop a test to determine the desired properties of the mixture in the context for which it is intended. This provides valuable information for specific project applications and can also help determine the general characteristics of a pozzolana for cases where the application of the pozzolana is not specified. This approach, along with that of fineness testing, forms the basis for most field tests.

Tests are required for a number of reasons;

1. To assess the viability of a new potential pozzolanic deposit

2. To provide quality control on a day-to-day basis as part of a production process

3. To provide long term quality control of the pozzolanic resource

Many of the standard tests specified in the relevant literature and in the national Standards which cover testing of pozzolanas (in India and USA for example), require sophisticated and expensive laboratory equipment to evaluate the pozzolanicity of a particular material. In developing countries where such equipment is beyond the reach of small-scale producers and where such laboratory facilities are often non-existent and many of the consumables hard to source, determining pozzolanicity can be a major problem. The time required to carry out such tests is also often very lengthy, often requiring a month or more for curing samples. This is not such a problem where the aim is to cover points 1 or 3 from the list above, but for short-term day-to-day analysis of the raw materials, a faster, simpler test is often required.

In this section, various test methods available for determining the reactivity of pozzolanas are described, those which are particularly suitable for use by small-scale users of pozzolanas in developing countries are highlighted. Standards available for testing pozzolans will be described.

2.4.1 Indian Standards

The Indian Standard for methods of Test for Pozzolanic Materials (2003) IS : 1727 - 1967 gives a variety of tests for determining various characteristics of pozzolanas. They are briefly described below.

1. Chemical analysis

The chemical analysis will determine the following characteristics for pozzolanas:

- Loss on ignition. This is the loss of weight due to release of volatiles on ignition. A sample is ignited in a furnace under controlled conditions and the weight loss measured. This applies to pozzolanas which have to be calcined for use.
- Silica content
- Combined ferric oxide and alumina content
- Ferric oxide content
- Alumina content
- Calcium oxide content
- Magnesia content
- Sulphuric anhydride content
- Determination of soluble salts

These chemical tests are performed using specified reagents. Results of chemical content are given as a weight percentage.

2. Fineness

- To determine the specific surface of the pozzolana - given in cm2/g
- To determine the fineness by sieving

3. Soundness

Soundness of a sample is a measurement of its tendency to crack, distort, pit or disintegrate. Either of the two following tests can be used to establish soundness:

- 'Le Chatelier' method uses a simple expandable ring to indicate the expansion of a sample over a set period of time
- The autoclave method. This method tests for expansion after a certain period of time at elevated temperature in an autoclave. The sample is prepared in

accordance with the Indian Standard for testing cement, but in place of cement a mixture of pozzolana and cement in the ratio 0.2N: 0.8 by weight is used, where,

N = Specific gravity of pozzolana/ Specific gravity of cement.

4. Initial and final setting time

Simple tests are carried out to determine the setting times for a lime-pozzolana and lime-cement sample. Apparatus used is called the Vicat set

5. Lime reactivity

The test for lime reactivity as given in these standards is very similar to the test for compressive strength. A series of 50mm cubes are prepared using a lime: pozzolana: sand mixture. They are allowed to cure for 8 days in an incubator and the compressive strength of the cubes is measured. Results are given in kg/cm^2.

6. Compressive strength

A similar test is carried out as for the lime reactivity given above, but the mix contains cement in place of lime. Compressive strength tests are carried out on specimens which have been incubated for 7, 28 and 90 days. A control test is also carried out using a pozzolana-free mixture. Three 50mm cubes are tested and the average figure used. Again the result is given in kg/cm^2.

7. Transverse strength

The transverse strength test is again similar to the compression strength test but in place of cubes rectangular block (160 x 40 x 40mm) are prepared and tested using specially designed equipment. The ratio of the pozzolana: cement: standard sand mix is 0.2N : 0.8 : 3 by weight (N is given above).

8. Drying shrinkage

A simple test on a 250 x 10 x 10mm block is used to deduce the shrinkage over a 7 and 35 day period.

9. Permeability

A specially designed 'permeability unit' is used to test a series of specimens for porosity. Water is forced under pressure through cured specimens and the passage of water measured. The resulting coefficient of permeability is given in cm/second/unit gradient.

10. Reduction in alkalinity and silica release

Only applicable to certain pozzolanas, this test helps to ascertain the effectiveness of some pozzolanas in reducing the harmful effects of alkali-aggregate reaction in concrete. It is a chemical test using reagents to determine the reduction in alkalinity, given in millimoles/liter.

11. Specific gravity

A simple measurement of the specific gravity of the raw pozzolana is using a piece of apparatus known as the 'Le Chatelier' flask. Given in g/ ml.

The above test procedure will give a comprehensive characterization of any pozzolana. The equipment required to perform such testing is, however, very costly and sophisticated. It is simply not possible in some regions of the world to carry out such tests, and where the application of the pozzolana is such that knowledge of the characteristics on such a level is not critical, then tests of this complexity are not suitable or necessary.

The Indian Standard 'Specification for Lime-Pozzolana Mixture' (IS 4098 - 1967) stipulates specific characteristics of different grades of such a mixture in terms of maximum free moisture content, loss on ignition and proportion retained on a 150

micron sieve; initial and final setting times; compressive strength and moisture retention. The minimum 28 day compressive strength, for example, is specified at between 7 and 40 kg/cm^2 depending on grade of material.

2.4.2 American Society for Testing and Materials (ASTM) Standard

The ASTM Standard (ASTM C311 - 77) varies slightly in content from the Indian Standard. Below is given a brief summary of the test methods of the ASTM standard.

Chemical analysis

1. Moisture content

This is determined by drying a sample in an oven and weighing to determine the percentage weight loss.

2. Loss on ignition

The method is similar to that used in the Indian Standard

3. Chemical content

- Silicon dioxide
- Aluminum oxide and iron oxide
- Calcium oxide
- Magnesium oxide
- Sulfur trioxide
- Available alkalis

As with the Indian Standard, these tests are carried out using specified reagents and the result is given as a percentage of the total weight.

Physical tests

4. Specific gravity

Specific gravity is measured using the 'Le Chatelier' flask.

5. Fineness

Fineness is calculated after wet sieving a sample of pozzolana on a No. 325 (45ìm) sieve.

6. Soundness

Soundness of a sample is a measurement of its tendency to crack, distort, pit or disintegrate. The autoclave method is used. This method tests for expansion after ascertain period of time at elevated temperature in an autoclave.

7. Drying shrinkage

Again 3 specimens (3 of mortar and 3 of concrete) are incubated and measured for shrinkage after 8, 16, 32 and 64 weeks. Length change data, reported as percent increase or decrease in linear dimension to the nearest 0.001% is based on an initial measurement made at the time of removal from the moulds.

8. Limits on amount of air-entraining admixture in concrete

Tests are carried out on hardened concrete containing a specified (neutralized Vinsol resin) air-entraining admixtures for compressive strength, flexural strength, resistance to freezing and thawing and length change.

9. Air entrainment of mortar

Calculation of the amount of air-entraining admixture required to produce a specified air content in mortar.

10. Pozzolanic activity index with Portland cement

The pozzolanicity index is a number based on the compressive strength of sample cubes such that:

Pozzolanicity activity index with Portland cement = A/B x 100

where, A is the average compressive strength of test mix cubes containing pozzolana (kPa), and

B is the average compressive strength of pozzolana free test cube mix (kPa)

11. Water requirement

Determination of water required to produce a specified flow in a pozzolana mix.

12. Pozzolanic activity index with lime

Similar to the test for pozzolanicity index with Portland cement but using lime. Based

on the compressive strength of the cured lime-pozzolana mix.

13. Reactivity with cement alkalis

Tests to determine the expansion of mortar due to the alkali-aggregate reaction.

2.4.3 British Standards

The British Standards Institute has no specific test to determine the reactivity of pozzolanic material. There is however a test for determining the pozzolanicity of pozzolanic cements BS EN 196-5 (1995).

Using the Rio-Fratini method, the pozzolanicity is assessed by comparing the quantity of calcium hydroxide in the aqueous solution in contact with the hydrated cement, after a fixed period of time, with the quantity of calcium hydroxide capable of saturating a solution of the same alkalinity. The test is considered positive if the concentration of calcium hydroxide in the solution is lower than the saturation concentration

2.5 Corn Cob

Corn or Maize, is a common name for the cereal grass widely grown for food and livestock fodder. Corn ranks with wheat and rice as one of the world's chief grain crops, and it is the largest crop of the United States. Corn is classified as *Zea mays*. The perennial wild corn thought to be extinct and rediscovered in Mexico is classified as *Zea diploperennis.*

According to the Food and Agriculture Organisation (FAO), maize production in Nigeria has risen from 7.1 million tons in 2006 to 7.8 million tons in 2007. Corn is native to the Americas and was the staple grain of the region for many centuries before Europeans reached the New World. The origin of corn remains a mystery. Conclusive evidence exists, from archaeological and paleobotanical discoveries that cultivated corn has existed in the southwestern United States for at least 3,000 years. Wild corn was once thought to have existed in the Tehuacán Valley of southern Mexico 7,000 years ago. More recent evidence puts the appearance of corn in that region at a much later date, about 4,600 years ago. Early wild corn was not much different in fundamental botanical characteristics from the modern corn plant.

The many varieties of corn show widely differing characteristics. Some varieties mature in 2 months; others take as long as 11 months. The foliage varies in intensity of color from light to dark green, and it may be modified by brown, red, or purple pigments. Mature ears vary in length from less than 7.5 cm (3 in) to as much as 50 cm (20 in).

World output of corn at the beginning of the 21st century was about 603 million metric tons annually; in volume of production, corn ranked first, ahead of rice and wheat. A net gain of about 51 percent in production was realized during the last two decades; intensive cultivation with heavy use of fertilizer and herbicides was

responsible for the increase. The United States is the leading corn-growing country, with about 40 percent of the world's production.

Approximately three-fifths of the corn sold by farmers is used as livestock feed. About half of that amount is fed directly to hogs, cattle, and poultry, and the rest is used in mixed feeds. Another one-fifth of U.S. corn is exported; the remaining one-fifth is sold as food and taken by commercial users for the production of alcohol and distilled spirits, syrups, sugar, cornstarch, and dry-process foods Policy Analysis Report No. 02-01 (2002).

Corncobs are an important source of furfural, a liquid used in manufacturing nylon fibers and phenol-formaldehyde plastics, refining wood resin, making lubricating oils from petroleum, and purifying butadiene in the production of synthetic rubber. Ground corncobs are used as a soft-grit abrasive. Large, whole cobs from a special type of corn, "cob pipe" corn, are used for pipes for smoking tobacco. Corn oil, extracted from the germ of the corn kernel, is used as a cooking and salad oil and, in solidified form, as margarine; it is also used in the manufacture of paints, soaps, and linoleum. The search for alternate sources of energy has brought attention to corn as a fuel source. High in sugar content, corn is processed to produce alcohol for use with gasoline as gasohol, and the dry stalk is a potentially important fuel biomass (Corn Investment Guide for Central) Visayas (2007).

Corn Cob is used for many purposes one of which is Corn Cob Abrasive. This is a tan colored, granular product made from the hard woody ring of a corn cob. Corn Cob Abrasive is used to de-burr (to remove rough edge from a piece of metal or other piece of work), burnish (polish metal until it shines), and polish a wide variety of products these include: Engine parts, ball bearings, nuts and bolts, springs, electric parts, generators and rotors, cutlery, jewelry, computer chips, fiberglass, and aluminum. Other

uses are cleaning of fire/smoke damage and cleaning of wooden houses/barns before painting.

Corn cob comprises three natural parts: the chaff and the pith forming the light part and the woody ring which forms the hard part of the cob.

Ash is the residue of burned plant parts like; bark, wood, sawdust, leaves, woody debris, pulp, husk, hulls, fronds, and other plant debris. Ash has been used for soil liming and for traditional pest control to some crawling pests (Stoll, 2000). Corn Cob Ash is obtained from the residue of combusted Corn cobs.

2.6 Portland Cement

Portland cement is produced by pulverizing clinker which consists primarily of hydraulic calcium silicates. Clinker also contains some calcium aluminates and calcium aluminoferrites, and one or more forms of calcium sulfate (gypsum) is inter-ground with the clinker to make the finished product. Materials used in the manufacture of Portland cement must contain appropriate amounts of calcium, silica, alumina, and iron components. During manufacture, chemical analyses of all materials are made frequently to ensure uniformly high quality cement. While the operations of all cement plants are basically the same, no flow diagram can adequately illustrate all plants. There is no typical Portland cement manufacturing facility and every plant has significant differences in layout, equipment, or general appearance (Gillberg et. al, 1999)

Selected raw materials are transported from the mine quarry, crushed, milled, and proportioned so that the resulting mixture has the desired chemical composition. The raw materials are generally a mixture of calcareous (calcium carbonate bearing) material, such as limestone, and an argillaceous (silica and alumina) material such as

clay, shale, fly ash, natural pozzolan or blast-furnace slag. Either a dry or wet process is used. In the dry process the grinding and blending are done with dry materials. In the wet process, the grinding and blending operations are done with the materials mixed with water in a slurry form. In other respects, the dry and wet processes are very much alike. Important technological developments have taken place in recent times that has improved significantly the productivity and energy efficiency of dry-process plants. After blending, the ground raw material is fed into the upper end of a kiln where the raw mix passes through the kiln at a rate controlled by the s1ope and rotational speed of the kiln. Burning fuel (powdered coal, new or recycled oil, natural gas, rubber tires, and byproduct fuel) is forced into the lower end of the kiln where temperatures of 1400'C to 1550°C change the raw material chemically into cement clinker of grayish-black pellets predominantly the size of marbles. The clinker is cooled and then pulverized. During this operation a small amount of gypsum is added to regulate the setting time of the cement and to improve shrinkage and strength development properties. In the grinding mill, clinker is ground so fine that nearly all of it passes through a 45 micron (No. 325) sieve.

2.6.1 Portland cement clinker

Portland cement clinker is made by sintering a precisely specified mixture of raw materials (raw meal, paste or slurry) containing elements, usually expressed as oxides, CaO, SiO_2, Al_2O_3, Fe_2O_3 and small quantities of other materials. The raw meal, paste or slurry is finely divided, intimately mixed and therefore homogeneous.

Portland cement clinker is a hydraulic material which shall consist of at least two-thirds by mass of calcium silicates (3CaO _ SiO2 and 2CaO _ SiO2), the remainder consisting of aluminium and iron containing clinker phases and other compounds. The ratio by

mass (CaO)/ (SiO_2) shall be not less than 2.0. The content of magnesium oxide (MgO) shall not exceed 5.0 % by mass.

2.6.2 Types of Portland Cement

Portland cement clinker is made by sintering a precisely specified mixture of raw materials (raw meal, paste or slurry) containing elements, usually expressed as oxides, CaO, SiO_2, Al_2O_3, Fe_2O_3 and small quantities of other materials. The raw meal, paste or slurry is finely divided, intimately mixed and therefore homogeneous.

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Different types of Portland cement are manufactured to meet various physical and chemical requirements for specific purposes. Portland cements are manufactured to meet the specifications of ASTM C 150 or ASTM C 1157. ASTM C 150 is the Standard Specification for Portland Cement and provides for eight types of Portland cement using Roman numeral designations as follows: -

Type 1: Normal.

Type IA: Normal, air-entraining.

Type II: Moderate sulfate resistance.

Type IIA: Moderate sulfate resistance, air-entraining.

Type III: High early strength.

Type IIIA: High early strength, air-entraining.

Type IV: Low heat of hydration.

Type V: High sulfate resistance.

BS 197 part 1 groups cements into five main cement types as follows;

- CEM I Portland cement;
- CEM II Portland-composite cement;
- CEM III Blast furnace cement;
- CEM IV Pozzolanic cement;
- CEM V Composite cement.

2.7 Concrete

Concrete is basically a mixture of two components: aggregates and paste. The paste, comprised of portland cement and water, binds the aggregates (usually sand and gravel or crushed stone) into a rocklike mass as the paste hardens because of the chemical reaction of the cement and water. Supplementary cementitious materials and chemical admixtures may also be included in the paste. The paste is composed of cementitious materials, water, and entrapped air or purposely entrained air. The paste constitutes about 25% to 40% of the total volume of concrete. The absolute volume of cement is usually between 7% and 15% and the water between 14% and 21%. Air content in air-entrained concrete ranges from about 4% to 8% of the volume

Aggregates make up about 60% to 75% of the total volume of concrete, their selection is important. Aggregates should consist of particles with adequate strength and resistance to exposure conditions and should not contain materials that will cause deterioration of the concrete. A continuous gradation of aggregate particle sizes is desirable for efficient use of the paste.

The quality of the concrete depends upon the quality of the paste and aggregate, and the bond between the two. In properly made concrete, each and every particle of aggregate is completely coated with paste and all of the spaces between aggregate particles are completely filled with paste (Neville, 2000)

For any particular set of materials and conditions of curing, the quality of hardened concrete is strongly influenced by the amount of water used in relation to the amount of cement. Unnecessarily high water contents dilute the cement paste (the glue of concrete).

Following are some advantages of reducing water content:

- Increased compressive and flexural strength
- Lower permeability, thus lower absorption and increased water-tightness
- Increased resistance to weathering
- Better bond between concrete and reinforcement
- Reduced drying shrinkage and cracking
- Less volume change from wetting and drying

The less water used, the better the quality of the concrete—provided the mixture can be consolidated properly. Smaller amounts of mixing water result in stiffer mixtures; but with vibration, stiffer mixtures can be easily placed. Thus, consolidation by vibration permits improvement in the quality of concrete (Neville, 2000).

The freshly mixed (plastic) and hardened properties of concrete may be changed by adding chemical admixtures to the concrete, usually in liquid form, during batching. Chemical admixtures are commonly used to;

(1) Adjust setting time or hardening,

(2) Reduce water demand,

(3) Increase workability,

(4) Intentionally entrain air,

(5) Adjust other fresh or hardened concrete properties.

After completion of proper proportioning, batching, mixing, placing, consolidating, finishing, and curing, concrete hardens into a strong, noncombustible, durable, abrasion-resistant, and watertight building material that requires little or no maintenance. Furthermore, concrete is an excellent building material because it can be formed into a wide variety of shapes, colors, and textures for use in an unlimited number of applications (Neville, 2000).

2.7.1 Mix Design

In the past, the specification for concrete prescribed the proportions of cement, and fine and coarse aggregate. Certain traditional mixes were thus produced but, owing to the variability of the mix ingredients, concretes having fixed cement-aggregate proportions and a given workability vary widely in strength. For this reason, the minimum compressive strength was later included in many specifications. This makes the specification unduly restrictive when good quality materials are available, but elsewhere it may not be possible to achieve an adequate strength using the prescribed mix proportions. This is why, sometimes, clauses prescribing the grading of aggregate and the shape of the particles have been added to the other requirements. However, the distribution of natural aggregates in many countries is such that these restrictions are often uneconomic. Furthermore, compliance with the requirements of strength, mix proportions, and aggregate shape and grading leaves no room for economies in the mix design, and makes progress in the production of cheap and satisfactory mixes on the basis of a study of the properties of concrete impossible (Neville, 2005).

It is not surprising, therefore, that the modern tendency is for specifications to be less restrictive. They lay down limiting values but often give also as a guide the traditional mix proportions for the benefit of the contractor who does not wish to use a high degree of control. The limiting values may cover a range of properties; the more usual ones are:-

1. "Minimum" compressive strength necessary from structural considerations;
2. Maximum water/cement ratio and/or maximum cement content. in certain conditions of exposure a minimum content of entrained air give adequate durability; .
3. Maximum cement content to avoid cracking due to the temperature.
4. Maximum cement content to avoid shrinkage cracking.
5. Minimum density for gravity dams and similar structures.

These various requirements must then be satisfied in the mix design calculations and they form, in fact, the basis of selection and proportioning of mix ingredients.

The British Code of Practice for the Structural Use of Concrete CP 110 (1972) has moved further than its predecessors towards this approach, i.e. to the use of designed mixes. These are virtually the norm nowadays. On the other hand, standard mixes (prescribed in the code by quantities of the dry ingredients per cubic meter and by slump may be used only on very small jobs, when the 28-day strength of concrete does not exceed 30 MPa and when no admixture or air entrainment is used.

It should be explained that a design in the strict sense of the word is not possible: the materials used are essentially variable and many of their properties cannot be assessed truly quantitatively. So that we are really making no more than an intelligent guess at the optimum combinations of the ingredients on the basis of the

relationships established. It is not surprising, therefore, that in order to obtain a satisfactory mix we not only have to calculate or estimate the proportions of the available materials but must also make trial mixes. The properties of these mixes are checked and adjustments in the mix proportions are made further trial mixes are made until a fully satisfactory mix is obtained.

2.7.2 Workability

The ease of placing, consolidating, and finishing freshly mixed concrete and the degree to which it resists segregation is called workability. Concrete should be workable but the ingredients should not separate during transport and handling. The degree of workability required for proper placement of concrete is controlled by the placement method, type of consolidation, and type of concrete. Different types of placements require different levels of workability. Factors that influence the workability of concrete are:

(1) The method and duration of transportation.

(2) Quantity and characteristics of cementitious materials.

(3) Concrete consistency (slump).

(4) Grading, shape, and surface texture of fine and coarse aggregates;

(5) Entrained air.

(6) Water content.

(7) Concrete and ambient air temperatures.

(8) Admixtures.

A uniform distribution of aggregate particles and the presence of entrained air significantly help control segregation and improve workability.

Properties related to workability include consistency, segregation, mobility, pumpability, bleeding, and finishability. Consistency is considered a close indication of workability. Slump is used as a measure of the consistency or wetness of concrete. A low-slump concrete has a stiff consistency. If the consistency is too dry and harsh, the concrete will be difficult to place and compact and larger aggregate particles may separate from the mix. However, it should not be assumed that a wetter, more fluid mix is necessarily more workable. If the mix is too wet, segregation and honeycombing can occur. The consistency should be the driest practicable for placement using the available consolidation equipment Neville (2005).

2.7.3 Hydration, Setting Time, and Hardening

The binding quality of Portland cement paste is due to the chemical reaction between the cement and water, called hydration. Portland cement is not a simple chemical compound, it is a mixture of many compounds. Four of these make up 90% or more of the weight of portland cement: tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite. In addition to these major compounds, several others play important roles in the hydration process. Each type of portland cement contains the same four major compounds, but in different proportions.

The two calcium silicates, which constitute about 75% of the weight of portland cement, react with water to form two new compounds: calcium hydroxide and calcium silicate hydrate. The latter is by far the most important cementing component in concrete. The engineering properties of concrete—setting and hardening, strength, and dimensional stability—depend primarily on calcium silicate hydrate. It is the heart of concrete. The chemical composition of calcium silicate hydrate is somewhat variable, but it contains lime (CaO) and silicate (SiO_2) in a ratio on the order of 3 to 2. The

surface area of calcium silicate hydrate is some 300 square meters per gram. In hardened cement paste, the calcium silicate hydrate forms dense, bonded aggregations between the other crystalline phases and the remaining un-hydrated cement grains; they also adhere to grains of sand and to pieces of coarse aggregate, cementing everything together (Copeland *et al*. 1962).

As concrete hardens, its gross volume remains almost unchanged, but hardened concrete contains pores filled with water and air that have no strength. The strength is in the solid part of the paste, mostly in the calcium silicate hydrate and crystalline compounds. The less porous the cement paste, the stronger the concrete. When mixing concrete, therefore, no more water than is absolutely necessary to make the concrete plastic and workable should be used. Even then, the water used is usually more than is required for complete hydration of the cement. About 0.4 grams of water per gram of cement are needed to completely hydrate cement (Powers 1948 and
1949). However, complete hydration is rare in field concrete due to a lack of moisture and the long period of time (decades) required to achieve complete hydration. Knowledge of the amount of heat released as cement hydrates can be useful in planning construction. In cold temperatures, the heat of hydration will help protect the concrete against damage from freezing temperatures. The heat may be harmful, however, in massive structures such as dams because it may produce undesirable temperature differentials. Knowledge of the rate of reaction between cement and
water is important because it determines the rate of hardening. The initial reaction must be slow enough to allow time for the concrete to be transported and placed. Once the concrete has been placed and finished, however, rapid hardening is desirable. Gypsum, added at the cement mill when clinker is ground, acts as a regulator of the initial rate of setting of portland cement. Other factors that influence the rate of hydration include

cement fineness, admixtures, amount of water added, and temperature of the materials at the time of mixing.

2.7.4 Strength

Compressive strength may be defined as the measured maximum resistance of a concrete specimen to axial loading. It is generally expressed in megapascals (MPa) or Newton per square meter (N/M^2) at an age of 28 days. One megapascal equals the force of one Newton per square millimeter (N/mm^2) or 1,000,000 N/m^2. Other test ages are also used; however, it is important to realize the relationship between the 28-day strength and other test ages. Seven-day strengths are often estimated to be about 75% of the 28-day strength and 56-day and 90-day strengths are about 10% to 15% greater than 28-day strengths. The compressive strength that a concrete achieves, results from the water-cement ratio (or water-cementitious materials ratio), the extent to which hydration has progressed, the curing and environmental conditions, and the age of the concrete. The relationship between strength and water-cement ratio has been studied since the late 1800s and early 1900s (Feret (1897) and Abrams (1918)). The strength of concrete increase as the water-cement ratio decreases. These factors also affect flexural and tensile strengths and bond of concrete to steel.

For a given workability and a given amount of cement, air-entrained concrete requires less mixing water than nonair- entrained concrete. The lower water-cement ratio possible for air-entrained concrete tends to offset the somewhat lower strengths of air-entrained concrete, particularly in lean to medium cement content mixes.

To determine compressive strength, tests are made on specimens of mortar or concrete. Unless otherwise specified, compression tests of mortar are made on 150-mm cubes, while compression tests of concrete are made on cylinders 150 mm diameter and

300 mm. Compressive strength of concrete is a primary physical property and frequently used in design calculations for bridges, buildings, and other structures.

The flexural strength or modulus of rupture of concrete is used to design pavements and other slabs on ground. Compressive strength, which is easier to measure than flexural strength, can be used as an index of flexural strength, once the empirical relationship between them has been established for the materials and the size of the element involved. The flexural strength of normal-weight concrete is often approximated as 0.7 to 0.8 times the square root of the compressive strength in megapascals (7.5 to 10 times the square root of the compressive strength). Wood (1992) illustrates the relationship between flexural strength and compressive strength for concretes exposed to moist curing, air curing, and outdoor exposure.

The direct tensile strength of concrete is about 8% to 12% of the compressive strength and is often estimated as 0.4 to 0.7 times the square root of the compressive strength in megapascals (5 to 7.5 times the square root of the compressive strength). Splitting tensile strength is 8% to 14% of the compressive strength (Hanson, 1968). Splitting tensile strength versus time is presented by Lange (1994).

The torsional strength for concrete is related to the modulus of rupture and the dimensions of the concrete element. Hsu (1968) presents torsional strength correlations. Shear strength–compressive strength relationships are discussed in the ACI 318 building code. The correlation between compressive strength and flexural, tensile, torsional, and shear strength varies with concrete ingredients and environment. Modulus of elasticity, denoted by the symbol E, may be defined as the ratio of normal stress to corresponding strain for tensile or compressive stresses below the proportional limit of a material.

2.7.5 Density

Conventional concrete, normally used in pavements, buildings, and other structures, has a density (unit weight) in the range of 2200 to 2400 kg/m^3. The density of concrete varies, depending on the amount and density of the aggregate, the amount of air that is entrapped or purposely entrained, and the water and cement contents, which in turn are influenced by the maximum size of the aggregate. Reducing the cement paste content (increasing aggregate volume) increases density. In the design of reinforced concrete structures, the combination of conventional concrete and reinforcing steel is commonly assumed to weigh 2400 kg/m^3 (Neville, 2005).

The weight of dry concrete equals the weight of the freshly mixed concrete ingredients less the weight of mix water that evaporates into the air. Some of the mix water combines chemically with the cement during the hydration process, converting the cement into cement gel. Also, some of the water remains tightly held in pores and capillaries and does not evaporate under normal conditions. The amount of mix water that will evaporate from concrete exposed to ambient air at 50% relative humidity is about 1% to 3% of the concrete weight; the actual amount depends on initial water content of the concrete, absorption characteristics of the aggregates, and size and shape of the concrete element.

2.8 Acid Attack

Concrete is susceptible to acid attack because of its alkaline nature. The components of the cement paste break down during contact with acids. Most pronounced is the dissolution of calcium hydroxide which occurs according to the following reaction:

$$2\ HX + Ca(OH)_2 \longrightarrow CaX_2 + 2\ H_2O$$

(X is the negative ion of the acid)

The decomposition of the concrete depends on the porosity of the cement paste, on the concentration of the acid, the solubility of the acid calcium salts (CaX2) and on the fluid transport through the concrete. Insoluble calcium salts may precipitate in the voids and can slow down the attack. Acids such as nitric acid, hydrochloric acid and acetic acid are very aggressive as their calcium salts are readily soluble and removed from the attack front. Other acids such as phosphoric acid and humic acid are less harmful. Their calcium salts, due to their low solubility, inhibit the attack by blocking the pathways within the concrete such as interconnected cracks, voids and porosity. Sulphuric acid is very damaging to concrete as it combines an acid attack and a sulfate attack (Experts International, 2006).

An acid attack is diagnosed primarily by two main features:

(1) Absence of calcium hydroxide in the cement paste

(2) Surface dissolution of cement paste exposing aggregates

Acids can attack and leach away the calcium compounds of cement paste formed in concrete through the hydration process, as well as the calcium in calcareous aggregate. The reaction is primarily between the offending acid and calcium hydroxide. Acid attack weakens the concrete structurally and reduces its durability and service life.

Acids can come from sources external to the concrete such as the earth surrounding a concrete structure, groundwater, rainwater, and pollutants in the air. Certain aggregates, including siliceous (silica-containing), will not be attacked by acid, but calcareous (calcium-containing) aggregates readily react with acids. In this way,

calcareous aggregates actually protect the concrete. Acids attack the paste and aggregate equally, spreading and lessening the damage to the paste (Kosmatka, 2002).

The pH of the acidic fluid and how much of it is in contact with the concrete are the primary determining factors in how corrosive the acid attack is. Acids are substances with a pH value lower than 7 (on a scale from 0 to 14). At a pH of about 6, some corrosive damage may be observed but it is superficial and only a real danger to concrete structures such as thin-walled piping and highly permeable concrete surfaces (St. John, 1998). In order for acid to attack and cause potentially serious damage, a pH of 5 or lower is usually required. The quantity of the acid will determine how much deterioration occurs (John, 1998).

2.8.1 Acidic Ground Water

Natural waters usually have pH values ranging anywhere from 5 to 8.5. Sometimes the pH can be as low as 4, but this is probably due to the presence of humic acid. Humic acid is organic residue from decaying organic matter. It is not dangerous to concrete because of its low solubility (Concrete Experts, 2002).

Groundwater that flows over and through decaying organic matter can take up carbon dioxide. This can lead to a decrease in pH and can cause attack that will carbonate the cement paste and calcium carbonate, dissolving the paste. This attack involves carbonic acid (H_2CO_3) and calcium bicarbonate, which is $Ca(HCO_3)_2$

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O$$

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaC0_3 + 2H_2O$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$$

Hydrated cement + H_2CO_3 -> intermediates -> Si hydrates + Al hydrates + Fe hydrates

The products of this reaction are silica and alumina gels as well as iron hydroxides. But these are side products to the real cause of deterioration, which is removal of formed soluble calcium bicarbonate by moving water (St. John, 1998).

2.8.2 Mineral Acids

Hydrochloric, nitric, sulfuric, chloric (found in chlorate salts), and chromic acids are known to be some of the most dangerous to concrete (Zivica, Bajza, 2001). These mineral acids, as they attack the calcium in the paste, can cause the formation of calcium salts. If the solubility of these salts is low enough, one of two things may happen. The first possibility is that the salts can form a protective layer on the surface, keeping further acid attack from occurring. This is the case in the instances of hydrofluoric and oxalic acid attack. The other possibility is that under attack by sulfuric acid, these salts will form expansive products such as ettringite and gypsum. This will increase the damage caused by acid and add to it cracking and delamination due to expansion (Zivica *et al*, 2001). Sulfate-rich environments can lead to the formation of sulfuric acid from sulfate by the action of bacteria.

2.8.3 Organic Acids

Organic acids come from wastewater or decayed plant life. These acids typically are a problem in grain silos and fruit storage facilities, livestock facilities, and wastewater treatment plants. In general, the aggressiveness of organic acids increases as the solubility of their calcium salts into the concrete pore structure increases (Zivica *et al*, 2001). Concrete floors in pig houses are attacked by lactic and acetic acids produced from meal-water mixtures spilled onto the floor. These acids combine with free lime

($Ca(OH)_2$) in the concrete, producing highly soluble calcium salts. These salts enter the pore structure of the concrete, lowering the pH of the pore solution and allowing corrosion of the paste. This process, along with the action of the hooves of livestock wearing on the weakened concrete, damages the floor (De Belie *et al*, 1997).

2.8.4 Industrial Pollutants

Industrial acidic attack can come from chemicals not found naturally or which have concentrations heightened from industrial activity. CO_2, SO_2, NO, NO_2, and NO_3 from industrial output can all reach high airborne concentrations in certain geographical areas, such as downwind of large cities and industrial sectors. Chlorides from marine environments may also be found in the atmosphere. All of these compounds can combine with water to form particles that fall to earth in the form of rain, fog, snow or dust (Zivica *et al,* 2001).

Acid rain has become a major contributor to acid attack in recent years. Increased emissions from industry, from the internal combustion engine, and from volcanic activity all add sulfur dioxide to the atmosphere, which later becomes sulfuric acid (Kosmatka, 2002).

2.8.5 Ways to Resist Acid Attack

Concrete is an alkaline material, with a pH above 12.5 necessary for proper strength and protection. Although this pH level makes concrete open to react with acidic compounds, the pH must be kept high in order to prevent corrosion from occurring. Keeping a low water/cement ratio will increase the resistance of the concrete to deterioration by acid. Low permeability, a result of the low water/cement ratio, will help keep the acidic solution out of the concrete pore structure (Kosmatka, 2002).

Certain admixtures help concrete to resist acid attack. Fly ash and silica fume, for example, have both been shown in studies to increase resistance to corrosion by acetic, lactic, and nitric acids (De Belie, *et al,* (1997); Pavlik (1997)). Cement paste containing fly ash contains less calcium hydroxide, $Ca(OH)_2$, than portland cement alone. Since calcium hydroxide is especially vulnerable to attack by acid, resistance increases. Also, smaller pores and a more homogeneous paste are found when fly ash is added to the cement mix (De Belie *et al,* (1997). Silica fume has a similar effect.

2.8.6 Sulphate Attack

The deterioration of mortar and concrete due to sulphate bearing soils has been well established. Naturally occurring sulphates of sodium, potassium or magnesium can chemically attack hardened cementitious materials in mortars and concrete, causing deterioration. To produce significant attack, aggressive chemicals have to be in solution and should be able to penetrate into the structure (Reading, 1982).

Sulphate attack is a complex process involving a sequence of different chemical reactions. There are mainly two mechanisms related to sulphate attack: ettringite and gypsum formation. In general, it is accepted that expansion and cracking are associated with ettringite formation. Strength loss and mass loss are associated with gypsum formation (Mehta, 1983). Also there is evidence that gypsum formation can cause considerable expansion when formed in large masses (Cao *et al* (1997), Glasser (1998)). However, gypsum formation is generally accompanied by a reduction in strength (Cao *et al,* 1997). Also, a third mechanism could take place as a result of decalcification of calcium silicate hydrates (C-S-H), or even un-hydrated C3S and β-C2S in the presence of sulphate ions (Gollop *et al* (1992); Mehta (1983)). Calcium ions are released to the pore solution and supply Ca2+ to promote the formation of either ettringite or gypsum.

It must be noted that the decalcification of C-S-H can also lead to loss of strength and elastic properties due to a reduction in binding capacity. Although this reaction is more predominant in acidic conditions, it can also occur in alkaline conditions (below pH 10) when both gypsum formation and decalcification could take place. It was noted that C-S-H around massive gypsum formation has very low calcium to silicon ratio. This type of attack, gypsum formation and decalcification of calcium silicates hydrates will lead to expansion and strength loss.

It has been discovered that integration supplementary cementing materials like fly ash, silica fume, blast—furnace slag and other pozzolanic materials would be able to reduce the amount of calcium hydroxide because of the pozzolanic reaction that took place finally increasing the resistance of the concrete to sulphate attack. The inclusion of pozzolanic materials in increasing the resistance to sulphate attack is well documented in the literature. Many pozzolans have been found that can effectively double the service life of a concrete when exposed to sulphate attack
(Harboe,1982). Research conducted by Mather (1982) and Yeginobali *et al.*(1996), although based on short-term studies suggest that silica fume has the potential to increase the resistance of concrete against sulphate attack. In addition, low-calcium fly ashes have been reported to be effective mineral admixtures for combating sulphate attack on concrete (Mehta, 1986).

2.8.6.1 Mechanism of Sulphate Attack

Calcium Hydroxide and Alumina-bearing phase of hydrated cement are more vulnerable to attack by Sulphate ions. Ettringite and Gypsum are the primary products of the chemical reaction between a Sulphate bearing solution and cement hydration products. Failure by expansion of concrete in the presence of Sulphate is due to the

formation of Ettringite. The attack of Sodium Sulphate on concrete is due to two principal reactions:

1. The reaction of Sodium Sulphate [Na_2SO_4] or Magnesium Sulphate [$MgSO_4$] and Calcium Hydroxide [(Ca(OH)2] to form Gypsum (Equations 1 and 2) and
2. The reaction of the formed Gypsum with Calcium Aluminate Hydrates to form Ettringite (Equation 3).

In addition to above, the Magnesium Sulphate reacts with all cement compounds, including Calcium Silicate Hydrates [C-S-H] and subsequently forming Gypsum and Ettringite (Equation 4). The Magnesium Hydroxide reacts with silica gel to form Magnesium Silicate Hydrate [M-S-H], being a soft material and affects the strength and durability of concrete. The form of Ettringite developed in the cement paste is depending on phase of Calcium Aluminate Hydrates, which reacts with Sulphate. In the fresh concrete, the Gypsum, which is blended to prevent flash set, reacts with Calcium Aluminate Hydrates to form primary Ettringite [$C_3As_3H_{32}$]. This primary Ettringite is converted to Monosulphate [C_3AsH_{32}] with time (James *et. al* 1998).

The chemical reactions associated with Sulphate attack are as follows:

$$Na_2SO_4 + Ca(OH)_2 + 2\ H_2O \Rightarrow CaSO_4.\ 2\ H_2O + 2\ NaOH \text{ ------(1)}$$

$$MgSO_4 + Ca(OH)_2 + 2\ H_2O \Rightarrow CaSO_4.\ 2\ H_2O + Mg(OH)_2 \text{ ------(2)}$$

(Gypsum)

$$3CaO.\ Al_2O_3\ .12H_2O + 3(CaSO_4.\ 2\ H2O) + 13H_2O \Rightarrow 3CaO.Al_2O_3\ .3CaSO_4.31H_2O \text{ -------(3)}$$

(Ettringite)

$$Mg\ SO_4 + C\text{-}S\text{-}H \Rightarrow CaSO_4.\ 2\ H_2O + M\text{-}S\text{-}H \text{ -------(4)}$$

2.8.7 Attack due to Chloride Salts

There are two basic transport mechanisms for the penetration of chlorides, diffusion of chloride ions and transport of chloride ion combined with water transport. Two parameters govern the chloride diffusion and the related risk of corrosion:

(a) Diffusion resistance of the concrete, which primarily depends on the pore size distribution and the chloride ion concentration gradient

(b) Binding capacity of the concrete with respect to chloride ions (both physical and chemical binding) as this binding capacity influences both the penetration rate and the ratio of bound to free chloride ions in the pore water.

The diffusion resistance of concrete to chloride ions is important as it governs the rate of penetration of chloride ions. Superior diffusion resistance (lower diffusion coefficient) would imply that it will take longer for chloride ion concentration at reinforcement to exceed a critical chloride concentration (C_{cr}), for which de-passivation and corrosion of the steel can take place. Thus concrete structures with high resistance to chloride diffusion are expected to have longer service life. Also the binding capacity of concrete is critical as it is generally recognized that only the free chloride ions in the pore water influences corrosion of reinforcement.

2.8.8 Assessment of Concrete for Acid Attack

Three modes of concrete deterioration are usually associated with Sulphate attack on concrete. The first mode of deterioration is due to eating away of the hydrated cement paste and leaving cohesion less granular mass. This mode of deterioration is known as acidic type and attributed mainly to the formation of Gypsum. The second mode of deterioration is due to the reaction of Sulphate to hydrated Aluminates phase,

forming Tricalcium Sulpho Aluminate Hydrate, also called Ettringite. This mode is expansion type and attributed mainly to the formation of Ettringite in the presence of high concentration of Calcium Hydroxide (Portlandite). The third type of deterioration is the onion-peeling type, which is characterized by scaling of concrete surface in successive layers (Marchand *et al.* 1999).

A visual inspection of concrete that has been attacked by acid should reveal corrosion of the paste that holds the aggregate in place. The aggregate may or may not be corroded, depending on whether it is siliceous or calcareous. Knowledge of the conditions of the surrounding environment will also help in diagnosing corrosion as being caused by acid.

A petro graphic study of a thin section can reveal evidence of acid attack on a concrete structure. The composition of the aggregate, cement type, w/c ratio, air void system, identification of admixtures, and surface flaws in the paste should all be determined (John, 1998).

2.8.9 Curing of Concrete

Curing is the maintenance of a satisfactory moisture content and temperature in concrete for a period of time immediately following placing and finishing so that the desired properties may develop. The need for adequate curing of concrete cannot be overemphasized.

Increase in strength with age continues provided;

(1) Unhydrated cement is still present,

(2) The concrete remains moist or has a relative humidity above approximately 80% (Powers 1948),

(3) The concrete temperature remains favorable,

(4) Sufficient space is available for hydration products to form.

Hydration and strength gain virtually stops when the relative humidity within the concrete drops to about 80%, or the temperature of the concrete drops below freezing. If concrete is re-saturated after a drying period, hydration is resumed and strength will again increase. However, it is best to moist-cure concrete continuously from the time it is placed until it has attained the desired quality; once concrete has dried out it is difficult to re-saturate (Neville, 2000).

Concrete must continue to hold enough moisture throughout the curing period for the cement to hydrate to the extent that desired properties are achieved. Freshly cast concrete usually has an abundance of water, but as drying progresses from the surface inward, strength gain will continue at each depth only as long as the relative humidity at that point remains above 80%.

Curing has a strong influence on the properties of hardened concrete. Proper curing will increase durability, strength, water-tightness, abrasion resistance, volume stability, and resistance to freezing and thawing and deicers. Exposed slab surfaces are especially sensitive to curing as strength development and freeze-thaw resistance of the top surface of a slab can be reduced significantly when curing is defective. When portland cement is mixed with water, a chemical reaction called hydration takes place. The extent to which this reaction is completed influences the strength and durability of the concrete. Freshly mixed concrete normally contains more water than is required for hydration of the cement; however, excessive loss of water by evaporation can delay or prevent adequate hydration. The surface is particularly susceptible to insufficient hydration because it dries first. If temperatures are favorable, hydration is relatively

rapid the first few days after concrete is placed; however, it is important for water to be retained in the concrete during this period, that is, for evaporation to be prevented or substantially reduced. With proper curing, concrete becomes stronger, more impermeable, and more resistant to stress, abrasion, and freezing and thawing. The improvement is rapid at early ages but continues more slowly thereafter for an indefinite period (Neville, 2000).

The most effective method for curing concrete depends on the materials used, method of construction, and the intended use of the hardened concrete. For most jobs, curing generally involves applying curing compounds, or covering the freshly placed and finished concrete with impermeable sheets or wet burlap. In some cases, such as in hot and cold weather, special care using other precautions is needed. Concrete mixtures with high cement contents and low water-cement ratios (less than 0.40) may require special curing needs. As cement hydrates (chemically combining with water) the internal relative humidity decreases causing the paste to self-desiccate (dry out) if no external water is provided. The paste can self-desiccate to a level where hydration stops. This may influence desired concrete properties, especially if the internal relative humidity

drops below 80% within the first seven days. In view of this, membrane-forming curing compounds may not retain enough water in the concrete. Therefore, fogging and wet curing become necessary to maximize hydration (Copeland *et al.* 1955). Fogging during and after placing and finishing also helps minimize plastic cracking in concretes with very low water-cement ratios (especially around 0.30 or less). When moist curing is interrupted, the development of strength continues for a short period and then stops after the concrete's internal relative humidity drops to about 80%. However, if moist curing

is resumed, strength development will be reactivated, but the original potential strength may not be achieved. Although it can be done in

a laboratory, it is difficult to re-saturate concrete in the field. Thus, it is best to moist-cure the concrete continuously from the time it is placed and finished until it has gained sufficient strength, impermeability, and durability. Loss of water will also cause the concrete to shrink, thus creating tensile stresses within the concrete. If these stresses develop before the concrete has attained adequate tensile strength, surface cracking can result. All exposed surfaces, including exposed edges and joints, must be protected against moisture evaporation. Hydration proceeds at a much slower rate when the concrete temperature is low. Temperatures below 10°C (50°F) are unfavorable for the development of early strength; below 4°C (40°F) the development of early strength is greatly retarded; and at or below freezing temperatures, down to -10°C (14°F), little or no strength develops.

2.8.9.1 Curing Methods and Materials

Concrete can be kept moist (and in some cases at a favorable temperature) by three curing methods:

1. Methods that maintain the presence of mixing water in the concrete during the early hardening period. These include ponding or immersion, spraying or fogging, and saturated wet coverings. These methods afford some cooling through evaporation, which is beneficial in hot weather.

2. Methods that reduce the loss of mixing water from the surface of the concrete. This can be done by covering the concrete with impervious paper or plastic sheets, or by applying membrane-forming curing compounds.

3. Methods that accelerate strength gain by supplying heat and additional moisture to the concrete. This is usually accomplished with live steam, heating coils, or electrically heated forms or pads.

The method or combination of methods chosen depends on factors such as availability of curing materials, size, shape, and age of concrete, production facilities (in place or in a plant), esthetic appearance, and economics. As a result, curing often involves a series of procedures used at a particular time as the concrete ages. For example, fog spraying or plastic covered wet burlap can precede application of a curing compound. The timing of each procedure depends on the degree of hardening of the concrete needed to prevent the particular procedure from damaging the concrete surface (ACI 308, 1997).

The compressive strength-developing behavior of concrete containing ash widely differs from that of concrete without ash depending on the method and amount of ash addition Goldman *et al* (1993), Sengul *et al.* (2002), Oner *et al.* (2005). The rate of strength increase of fly ash concrete is slower but it is sustained for longer periods than the rate of the strength increase of portland cement concrete Chindaprasirt *et al.* (2005), Hwang *et al.* (2004).

The strength development for various curing histories has been investigated with particular regard to the influences of curing time points with given temperatures. Four different points of curing time were considered with an individual interval of 24 hour. Two different temperatures of 5°C and 40°C were applied for the selective intervals, whereas the rest period days were under the reference curing condition of 20°C. Test results show that the concrete subjected to a high temperature at an early age attains higher early-age strength but eventually attains lower later-age strength. The concrete

subjected to a low temperature at an early age led to lower early-age strength but almost the same later-age strength. Kim *et al.* (1998).

Decades of in-depth research and field performance have proved beyond doubt that pozzolanic materials have potentials to enhance all the qualities of a concrete that it should exercise in its service life. Basically, inclusion pozzolanic materials in concrete manufacturing have been proven to be very effective, causing pore refinement of larger pores into fine ones, thereby, protecting the structure by preventing the ingress of harmful agents. However, the contribution of pozzolanic materials to durability and strength of concrete appears to be strongly dependent on the type and amount mixed with it, and the length of curing period. Therefore, careful mix design and proper casting and also curing method of blended cement concrete would be able to produce concrete of better durability and strength than the plain concrete.

2.9 British Standards

The British Standards Institute has no specific test to determine the reactivity of pozzolanic material. There is however a test for determining the pozzolanicity of pozzolanic cements (BS EN 196-5 (1995). BS EN 197-1(2000) also gives the following guidelines Pozzolanas consist essentially of reactive silicon dioxide (SiO_2) and aluminum oxide

(Al_2O_3). The remainder contains iron oxide (Fe_2O_3) and other oxides. The proportion of reactive Calcium oxide for hardening is negligible. The reactive silicon dioxide content shall be not less than 25.0 % by mass.

Other standard tests specified in the relevant literature and in the national Standards which cover testing of pozzolanas (in India and USA for example), require

sophisticated and expensive laboratory equipment to evaluate the pozzolanicity of a particular material.

However the following tests are an example of Standards developed by countries to allow accurate characterization of pozzolanic materials. Other countries apart from those mentioned below publish such Standards and these should be referred to where applicable. There are also even more sophisticated procedures used, such as x-ray diffraction or electron microscopy to determine whether the structure of a pozzolana is amorphous (more reactive with lime) or crystalline.

1. Chemical analysis

The chemical analysis will determine the following characteristics for pozzolanas:

- Loss on ignition. This is the loss of weight due to release of volatiles on ignition. the sample is ignited in a furnace under controlled conditions and the weight loss measured.
- Silica content
- Ferric oxide content
- Alumina content
- Calcium oxide content

These chemical tests are performed using specified reagents. Results of chemical content are given as a weight percentage. This result is presented in table 3.1 above.

2. Fineness

Fineness or particle size of CCA affects hydration rate. The smaller the particle size the greater the surface area-to-volume ratio, and thus, the more area available for water-cement interaction per unit volume. The method used to determine the fineness

was AASHTO T 128: Fineness of Hydraulic Cement by the 75-mm (No. 200) Sieves. The result for fineness of CCA is presented in the table 3.2 below.

2.10 Mechanical requirements

2.10.1 Standard strength

Cement paste strength is typically defined in three ways: compressive, tensile and flexural. These strengths can be affected by a number of items including: water-cement ratio, cement-fine aggregate ratio, type and grading of fine aggregate, manner of mixing and molding specimens, curing conditions, size and shape of specimen, moisture content at time of test, loading conditions and age (Mindess *et al.* 1981). Since cement gains strength over time, the time at which strength test is to be conducted must be specified. Typically times are 1 day (for high early strength cement), 3 days, 7 days, 28 days and 90 days (for low heat of hydration cement). Standard strength of cement is the compressive strength determined in accordance with EN 196-1 at 28 days and shall conform to the requirements in Table 2 of BS 197 part 1. Three classes of standard strength are included: class 32,5 class 42,5 and class 52,5 (see Table 3.5).

2.10.2 Early strength

The early strength of cement is the compressive strength determined in accordance with EN 196-1 at either 2 days or 7 days and shall conform to the requirements in Table 2 of BS 197 part 1(Table 3.3 below). Two classes of early strength are included for each class of standard strength, a class with ordinary early strength, indicated by N, and a class with high early strength, indicated by R

Table 2.2: Mechanical and physical requirements of cement given as characteristic values

Strength class	Compressive strength MPa				Initial setting time	Sound-ness (expan-sion)
	Early strength		Standard strength			
	2 days	7 days	28 days		min	mm
32.5 N	-	≥ 16.0	≥ 32.5	≤ 52.5	≥ 75	≤ 10
32.5 R	≥ 10.0	-				
42.5 N	≥ 10.0	-	≥ 42.5	≤ 62.5	≥ 60	
42.5 R	≥ 20.0	-				
52.5 N	≥ 20.0	-	≥ 52.5	-	≥ 45	
52.5 R	≥ 30.0	-				

2.10.3 Physical requirements

2.10.3.1 Setting time

Cement paste setting time is affected by a number of items including: cement fineness, water-cement ratio, chemical content (especially gypsum content) and admixtures. Setting tests are used to characterize how a particular cement paste sets. For construction purposes, the initial set must not be too soon and the final set must not be too late. Additionally, setting times can give some indication of whether or not cement is undergoing normal hydration (PCA, 1988). Normally, two setting times are defined (Mindess *et al.* 1981):

1. Initial set. Occurs when the paste begins to stiffen considerably.

2. Final set. Occurs when the cement has hardened to the point at which it can sustain some load.

These particular times are just arbitrary points used to characterize cement, they do not have any fundamental chemical significance. Both common setting time tests, the Vicat needle and the Gillmore needle, define initial set and final set based on the time at which a needle of particular size and weight either penetrates a cement paste sample to a given depth or fails to penetrate a cement paste sample. The Vicat needle test is more common and tends to give shorter times than the Gillmore needle test. The initial setting time, determined in accordance with EN 196-3, shall conform to the requirements in Table 2 BS 197 part 1(Table 3.3). Table 3.4 shows ASTM C 150 specified set times.

Table 2.3: ASTM C 150 Specified Set Times by Test Method

Test Method	Set Type	Time Specification
Vicat	Initial	≤45 minutes
	Final	≥375 minutes
Gillmore	Initial	≤60 minutes
	Final	≥600 minutes

2.10.3.2 Soundness

When referring to Portland cement, "soundness" refers to the ability of a hardened cement paste to retain its volume after setting without delayed destructive expansion (PCA, 1988).

Soundness means the ability or otherwise of a cement to maintain a constant volume. An unsound cement will expand slowly and over a long time. Its effect may not become apparent for some months but it is capable of causing severe cracking of the cracking and even eventual failure. Unsoundness is caused by the presence of excess gypsum or too high proportion of free lime or magnesia. As the lime and magnesia are calcined at high temperatures, they hydrate very slowly and the expansion takes place a long time

after the concrete has set. If un-sound cement is aerated carbon dioxide and moisture in the atmosphere will combine with any free lime or magnesia converting them into carbonates and hydroxides which are harmless. Under British standard specification cement which fails the test may be aerated and retested. If it then satisfies a more stringent requirement for expansion it may be accepted. Presumably in this event it would be wise to aerate all cement before use in the work. In soundness test heat is applied to the sample of cement in other to speed up the expansion which takes place if the cement is unsound.The expansion, determined in accordance with EN 196-3, shall conform to the requirement in table 2.

2.10.3.3 Chemical requirements

Portland cements can be characterized by their chemical composition although they rarely are for pavement applications. However, it is a portland cement's chemical properties that determine its physical properties and how it cures. Therefore, a basic understanding of portland cement chemistry can help one understand how and why it behaves as it does.

The properties of the cements of the cement type and strength class shown in columns 3 and 4 respectively of Table 2.5 shall conform to the requirements listed in column 5 of this table when tested in accordance with the standard referred to in column 2. Table 2.6 shows the main chemical compound constituents of portland cement.

Table 2.4: Chemical requirements of cement give as characteristic values (EN 197−1:2000

1	2	3	4	5
Property	**Test reference**	**Cement type**	**Strength class**	**Requirements** [a]
Loss on ignition	EN 196-2	CEM I CEM III	all	≤ 5,0 %
Insoluble residue	EN 196-2 [b]	CEM I CEM III	all	≤ 5,0 %
Sulfate content (as SO_3)	EN 196-2	CEM I CEM II [c] CEM IV CEM V	32.5 N 32.5 R 42.5 N	≤ 3,5 %
			42.5 R 52.5 N 52.5 R	≤ 4,0 %
		CEM III [d]	all	
Chloride content	EN 196-21	all [e]	all	≤ 0,10 % [f]
Pozzolanicity	EN 196-5	CEM IV	all	Satisfies the test

[a] Requirements are given as percentage by mass of the final cement.
[b] Determination of residue insoluble in hydrochloric acid and sodium carbonate.
[c] Cement type CEM II/B-T may contain up to 4,5 % sulfate for all strength classes.
[d] Cement type CEM III/C may contain up to 4.5 % sulfate.
[e] Cement type CEM III may contain more than 0,10 % chloride but in that case the maximum chloride content shall be stated on the packaging and/or the delivery note.
[f] For pre-stressing applications cements may be produced according to a lower requirement. If so, the value of 0,10 % shall be replaced by this lower value which shall be stated in the delivery note.

Table 2.5: Chemical Requirements given as characteristic Values (EN 197−1:2000)

1	2	3	4	5
Property	**Test reference**	**Cement type**	**Strength class**	**Requirements** [a]
Loss on ignition	EN 196-2	CEM I CEM III	all	≤ 5,0 %
Insoluble residue	EN 196-2 [b]	CEM I CEM III	all	≤ 5,0 %
Sulfate content (as SO_3)	EN 196-2	CEM I CEM II [c] CEM IV CEM V	32,5 N 32,5 R 42,5 N	≤ 3,5 %
			42,5 R 52,5 N 52,5 R	≤ 4,0 %
		CEM III [d]	all	
Chloride content	EN 196-21	all [e]	all	≤ 0,10 % [f]
Pozzolanicity	EN 196-5	CEM IV	all	Satisfies the test

a) Requirements are given as percentage by mass of the final cement.
b) Determination of residue insoluble in hydrochloric acid and sodium carbonate.
c) Cement type CEM II/B-T may contain up to 4,5 % sulfate for all strength classes.
d) Cement type CEM III/C may contain up to 4,5 % sulfate.
e) Cement type CEM III may contain more than 0,10 % chloride but in that case the maximum chloride content shall be stated on the packaging and/or the delivery note.
f) For pre-stressing applications cements may be produced according to a lower requirement. If so, the value of 0,10 % shall be replaced by this lower value which shall be stated in the delivery note.

Table 2.6: Main Constituents in a Typical Portland Cement (Mindess and Young, 1981)

Chemical Name	Chemical Formula	Shorthand Notation	Percent by Weight
Tricalcium Silicate	$3CaO \times SiO_2$	C_3S	50
Dicalcium Silicate	$2CaO \times SiO_2$	C_2S	25
Tricalcium Aluminate	$3CaO \times Al_2O_3$	C_3A	12
Tetracalcium Aluminoferrite	$4CaO \times Al_2O_3 \times Fe_2O_3$	C_4AF	8
Gypsum	$CaSO_4 \times H_2O$	CSH_2	3.5

2.11 Durability requirements

In many applications, particularly in severe environmental conditions, the choice of cement has an influence on the durability of concrete, mortar and grouts, e.g. frost resistance, chemical resistance and protection of reinforcement. The choice of cement, from EN 197-1, particularly as regards type and strength class for different applications and exposure classes shall follow the appropriate standards and/or regulations for concrete or mortar valid in the place of use (Roper *et al*, 1994).

Dangote brand of Portland cement was selected for use in this experiment. The cement used was Dangote Cement obtained from a major dealer. Dangote cement has been classified as an Ordinary Portland (Muhammad, 2006). Physical and chemical tests have been carried out on the cement in accordance to Nigerian Industrial Standards: NIS 445 (2003); NIS 446 (2003); NIS 447 (2003); NIS 448 (2003); NIS 449 (2003), NIS 455 (2003) and B.S. No. 12 Portland cement.

The fundamental tests for cement quality are those for setting time, soundness, strength, fineness and chemical composition. Physical tests carried out on the cement include consistency test, soundness test, and initial and final setting times. These tests were carried out to characterize and ensure the properties of cement used met the standard requirements of the code.

2.12 Water:

In many specifications, the quality of water is covered by a clause saying that water should be fit for drinking. Such water very rarely contains dissolved solids in excess of 2000 parts per million (ppm), and as a rule less than 1000 ppm. For a water/cement ratio of 0.5 by mass, the latter content corresponds to a quantity of solids equal to 0.05 per cent of the mass of cement, and thus any effect of the common solids

(considered as aggregate) would be small. If the silt content is higher than 2000 ppm, it is possible to reduce it by allowing the water to stand in a settling basin before use. However, water used to wash out truck mixers is satisfactory as mixing water (because the solids in it are proper concrete ingredients), provided of course that it was satisfactory to begin with. ASTM C 94-92a allows the use of wash water, but, obviously, different cements and different admixtures should not be involved. The criterion of portability of water is not absolute: drinking water may be unsuitable as mixing water when the water has a high concentration of sodium or potassium and there is a danger of alkali-aggregate reaction

Sea water (or any water containing large quantities of chlorides) tends to cause persistent dampness and efflorescence. Such water should not be used where appearance of the concrete is of importance or where a plaster finish is to be applied. In the case of reinforced concrete, sea water increases the risk corrosion of the reinforcement, especially in tropical countries. Corrosion has been observed in structures exposed to humid air when the cover to reinforcement is inadequate or the concrete is not sufficiently dense so that the corrosive action of residual salt in the presence of moisture can take place.

Generally, water satisfactory for mixing is also suitable for curing purposes. However, iron or organic matter may cause staining, particularly if water flows slowly over concrete and evaporates rapidly. In some cases, discoloration is of no significance, and any water suitable for mixing, or even slightly inferior in quality, is acceptable' for curing. However, it is essential that curing water be free from substances that attack hardened concrete. For example, concrete is attacked by water containing free CO_2. Flowing pure water, formed by melting ice or by condensation, and containing little CO_2, dissolves $Ca(OH)_2$ and causes surface erosion.

A simple way of determining the suitability of water for mixing is to compare the setting time of cement and the strength of mortar cubes using the water in question with the corresponding results obtained using known 'good' water or distilled water; there is no appreciable difference between the behavior of distilled and ordinary drinking water. BS 3148: 1980 suggests a tolerance of 10 per cent to allow for chance variations in strength. Such tests are also recommended when water, for which no service record is available, contains dissolved solids in excess of 2000 ppm, or, in the case of alkali carbonate or bicarbonate, in excess of 1000 ppm. When unusual solids are present these tests are also advisable. Whether or not staining will occur due to impurities in the curing water cannot be determined on the basis of chemical analysis and should be checked by a performance test involving simulated wetting and evaporation

2.13 Design and Manufacture of Concrete

Except for the tests involved in measuring the expansions of mortar, all the performance evaluation of CCA were accomplished with concrete specimens. Absolute volume mix design, and a coherent mix proportion based on fixed water-binder ratio with medium class cement content (368kg/m3) was selected with a target strength of 30N/mm^2. Water-binder ratio of 0.5 was used throughout the research and the mixing of ash in concrete was based on a simple approach of direct replacement. A relatively similar approach was adopted by Tay (1990) who used a 1:2:4 (cement sand: coarse aggregate) mix with a water-to-cement ratio of 0.6 for both OPC and oil-palm ash concrete. With a minimum water/(cement+ POFA) ratio of 0.55, however, Abu (1990) followed a mix proportion of 1:2:2 for cement, fine and coarse aggregates for the

manufacture of concrete. Concrete is designed to satisfy workability and strength in its fresh and hardened state conditions.

Modifications have been made in the concrete mixes, for Comparison purposes of the performance behavior of corn cob ash modified concretes with that of the control OPC. The only difference in the ash concrete is that 10%, 20 %, 30%, 40% and %0% OPC has been replaced by the same amount of corn cob ash. Cube specimens of 150 x 150mm size were prepared for testing normal and aggressive environments. The number of specimens for each mix condition and for each age of testing was also the same Awal et al (1997).

.2.14 Aggressive Environments

Aggressive environments are generated by human activities and by free acids in nature. ACI Committee Report 201 (2001) has classified chemical attacks into several types that include; acidic attack, alkali attack, carbonation, chloride attack, leaching and sulphate attack. It can be accepted as a general rule that acids are deleterious to concrete. The spectrum of aggressive acidic media is wide. Acidic attack usually originates from industrial processes, but it can even be due to urban activity. Even natural exposure conditions may cause acid attacks. Free acids in natural waters are rare. Exceptions are carbonic waters and sulphurous and Sulphuric acids in peat waters. Soils may contain huminous acids. Several organic and inorganic acids may occur in shallow regions of sea-water as a consequence of bacteriological activity. Significant quantities of free acids in plants and factories may be found. In these cases, the concentration of acid, which comes in contact with concrete structures, may reach to high values (Ecob *et al.* (1990); Baradan *et al.* (2002)).

The degree of aggressivity of an acid is dependent on the chemical character of anions present. The strength of acid, its dissociation degree in solutions and, mainly, the solubility of the calcium salts formed are dependent on the chemical character of anion. The acidic attack is affected by the processes of decomposition and leaching of the constituent of cement matrix (Gutt *et al.* (1997); Mehta (1986)).

The pH of the acidic fluid and how much of it is in contact with the concrete are the primary determining factors in how corrosive the acid attack is. Acids are substances with a pH value lower than 7 (on a scale from 0 to 14). At a pH of about 6, some corrosive damage may be observed but it is superficial and only a real danger to concrete structures such as thin-walled piping and highly permeable concrete surfaces (John, 1998). In order for acid to attack and cause potentially serious damage, a pH of 5 or lower is usually required. The quantity of the acid will determine how much deterioration occurs (John, 1998).

2.14.1 Mineral Acids

Hydrochloric, nitric, sulphuric, chloric (found in chlorate salts), and chromic acids are known to be some of the most dangerous to concrete (Zivica *et al.* 2001). These mineral acids, as they attack the calcium in the paste, can cause the formation of calcium salts. If the solubility of these salts is low enough, one of two things may happen. The first possibility is that the salts can form a protective layer on the surface, keeping further acid attack from occurring. This is the case in the instances of hydrofluoric and oxalic acid attack. The other possibility is that under attack by sulphuric acid, these salts will form expansive products such as ettringite and gypsum. This will increase the damage caused by acid and add to it cracking and delamination

due to expansion (Zivica *et al*. 2001). Sulphate-rich environments can lead to the formation of sulphuric acid from sulphate by the action of bacteria

2.14.2 Organic Acids

Organic acids come from wastewater or decayed plant life. These acids typically are a problem in grain silos and fruit storage facilities, livestock facilities, and wastewater treatment plants. In general, the aggressiveness of organic acids increases as the solubility of their calcium salts into the concrete pore structure increases (Zivica *et al.*2001). Concrete floors in pig houses are attacked by lactic and acetic acids produced from meal-water mixtures spilled onto the floor. These acids combine with free lime (Ca(OH)2) in the concrete, producing highly soluble calcium salts. These salts enter the pore structure of the concrete, lowering the pH of the pore solution and allowing corrosion of the paste. This process, along with the action of the hooves of livestock wearing on the weakened concrete, damages the floor (De Belie, et al, 1997).

2.14.3 Salts

Ettringite and Gypsum are the primary products of the chemical reaction between a Sulphate bearing solution and cement hydration products. Failure by expansion of concrete in the presence of Sulphate is due to the formation of Ettringite. The attack of Sodium Sulphate on concrete is due to two principal reactions: the reaction of Sodium Sulphate [Na2SO4] or Magnesium Sulphate [MgSO4] and Calcium Hydroxide [(Ca(OH)2] to form Gypsum and the reaction of the formed Gypsum with Calcium Aluminate Hydrates to form Ettringite. In addition to above, the Magnesium Sulphate reacts with all cement compounds, including Calcium Silicate Hydrates [C-S-H] and subsequently forming Gypsum and Ettringite.

Deterioration of concrete in Sulphate attack depends on concentration of Sulphate in exposure solution. Higher concentration of Sulphate leads to quick deterioration. Al-Dulaijan *et al.* (2003) studied the performance of plain and blended cement mortar cubes of 50 mm size, exposed to Sodium Sulphate solution of varying concentration (1.0, 1.5, 2.0, 2.5 and 4.0%) for up to 24 months. The degree of deterioration was evaluated by strength reduction and by visual inspection. Results of the study indicate that the rate of deterioration increased with increase in Sulphate concentration for both plain and blended cement

Aggressive solutions used in these experiments were classified into inorganic acids, organic acids and salt solutions. In this vain, sulphuric acid solution, acetic acid solution and magnesium sulphate solution were selected for the experiments. Concentrations of 5% and 10% of each of the solutions were used for the experiments.

2.14.4 Sulfuric acid

Sulfuric acid (sulphuric acid in British English) is a strong mineral acid with the molecular formula H_2SO_4. It is soluble in water at all concentrations. Sulfuric acid has many applications, and is one of the top products of the chemical industry. World production in 2001 was 165 million tones, with an approximate value of US$8 billion. Principal uses include lead-acid batteries for cars and other vehicles, ore processing, fertilizer manufacturing, oil refining, wastewater processing, and chemical synthesis.

Pure (undiluted) sulfuric acid is not encountered naturally on Earth, due to its great affinity for water. Apart from that, sulfuric acid is a constituent of acid rain, which is formed by atmospheric oxidation of sulfur dioxide in the presence of water i.e., oxidation of sulfurous acid. Sulfur dioxide is the main byproduct produced when sulfur-containing fuels such as coal or oil are burned (Hill *et al.* (2003)).

Sulfuric acid is formed naturally by the oxidation of sulfide minerals, such as iron sulfide. The resulting water can be highly acidic and is called acid mine drainage (AMD) or acid rock drainage (ARD). This acidic water is capable of dissolving metals present in sulfide ores, which results in brightly-colored, toxic streams.

2.15 Resistance to Acid Attack

Although various physical and chemical tests on the resistance of concrete to acids have been developed (Lea, 1970), but still there are no standard procedures can be followed. Acids of various types, viz, sulphuric acid, hydrochloric acid, acetic acid, nitric acid etc. are normally used in determining the performance of concrete in acidic environment. In the present investigation, concrete cube specimens having mix proportions similar to the ones specified in section 3.7.2.3 were prepared and cured in water for 28 days before putting them into 5 % and 10% acid solution. The durability performance of OPC and CCA/ OPC concrete specimens were then determined by periodic measurement of weight losses of the samples continuously immersed in the test solution. The concentration of the solutions was controlled by periodically renewing the strength of solutions every four weeks throughout the immersion period. Fault tree diagram showing the experimental design is shown in figure 2 below (Hill, J. et al. 2003).

Concrete cube specimens that have been put into solution were periodically subjected to visual inspection and mass change measurements. Mass change measurements were done after every 336 hours. Before each reading the specimens were carefully brushed and cleaned with water to remove salt from the surface. Prior to weighing, the specimens were brought to saturated surface dry condition. Following the mass measurement test, the concrete cube specimens were subjected to compression for

assessing residual strength. These test were performed at 60days and 90days after soaking in acid solutions. The companion OPC and CCA/ OPC cube specimens that were not exposed to acid attack, were also tested simultaneously to obtain a relative performance

2.16 Analysis of Variance Overview

In an experiment study, various treatments are applied to test subjects and the response data is gathered for analysis. A critical tool for carrying out the analysis is the **Analysis of Variance** (ANOVA). It enables a researcher to differentiate treatment results based on easily computed statistical quantities from the treatment outcome.

The variability in a set of data quantifies the scatter of the data points around the mean. To calculate a variance, first the mean is calculated, then the deviation of each point from the mean. Deviations will be both positive and negative; and the sum will be zero. (This follows directly from how the mean was calculated in the first place). This will be true regardless of the size of the dataset, or amount of variability within a dataset, and so the raw deviations are not useful as a measure of variability (Zar, 1996).

Analysis of variance (ANOVA) is similar to regression in that it is used to investigate and model the relationship between a response variable and one or more independent variables. However, analysis of variance differs from regression in two ways:

The independent variables are qualitative (categorical), and no assumption is made about the nature of the relationship (that is, the model does not include coefficients for variables). In effect, analysis of variance extends the two-sample t-test for testing the equality of two population means to a more general null hypothesis of

comparing the equality of more than two means, versus them not all being equal. Several of MINITAB's

ANOVA procedures, however, allow models with both qualitative and quantitative variables. MINITAB's ANOVA capabilities include procedures for fitting ANOVA models to data collected from a number of different designs, for fitting MANOVA models to designs with multiple responses, for fitting ANOM (analysis of means) models, and specialty graphs for testing equal variances, for error bar or confidence interval plots, and graphs

of main effects and interactions.

2.16.1 Sample Size

The sample size of a statistical sample is the number of observations that constitute it. It is typically denoted n, a positive integer. The sample size is an important feature of any empirical study in which the goal is to make inferences about a population from a sample. In practice, the sample size used in a study is determined based on the expense of data collection, and the need to have sufficient statistical power. In a census, data are collected on the entire population, hence the sample size is equal to the population size.

Larger sample sizes generally lead to increased precision when estimating unknown parameters. Several fundamental facts of mathematical statistics describe this phenomenon, including the law of large numbers and the central limit theorem. In some situations, the increase in accuracy for larger sample sizes is minimal, or even non-existent. This can result from the presence of systematic errors or strong dependence in the data, or if the data follow a heavy-tailed distribution (Design of Engineering Experiments Part 2).

The traditional approach to estimation of sample size is based on statistical significance of your outcome measure. You have to specify the smallest effect you want to detect, the Type I and Type II error rates, and the design of the study. I present here new formulae for the resulting estimates of sample size. I also include new ways to adjust for validity and reliability, and I finish with sample sizes required for several complex cross-sectional designs. I also advocate a new approach to sample-size estimation based on width of the confidence interval of your outcome measure. In this new approach, your concern is with the precision of your estimate of the effect, not with the statistical significance of the effect. The formulae on these pages still apply, but you halve the sample sizes (Axon, 1970).

Sample sizes are judged based on the quality of the resulting estimates. For example, if a proportion is being estimated, one may wish to have the 95% confidence interval be less than 0.06 units wide. Alternatively, sample size may be assessed based on the power of a hypothesis test. For example, if we are comparing the support for a certain political candidate among women with the support for that candidate among men, we may wish to have 80% power to detect a difference in the support levels of 0.04 units.

2.16.2 One-way and two-way ANOVA models

One-way analysis of variance tests the equality of population means when classification is by one variable. The classification variable, or factor, usually has three or more levels (one-way ANOVA with two levels is equivalent to a t-test), where the level represents the treatment applied. For example, if you conduct an experiment where you measure durability of a product made by one of three methods, these methods

constitute the levels. The one-way procedure also allows you to examine differences among means using multiple comparisons (Axon, 1970).

Two-way analysis of variance performs an analysis of variance for testing the equality of populations means when classification of treatments is by two variables or factors. In two-way ANOVA, the data must be balanced (all cells must have the same number of observations) and factors must be fixed (DeCoursey 2003).

2.17 Quality of Concrete.

To fully appreciate the benefits of ash in concrete, the basics of producing exceptional concrete must be understood. Concrete is a composite material, which essentially consists of two components: aggregates and cementitious paste. To produce exceptional concrete, it is extremely important to have a smooth gradation of material from rock down to the finest particles (in other words, a good mix of particle sizes, so that the largest practicable rock fills the majority of the volume, while the progressively smaller rock and sand fill the voids left between the larger particles). Ideally, it is best to have as much volume as possible filled with strong, durable aggregate particles, with enough paste (comprised of as much CSH and as little lime as possible) to coat every particle. Also, voids should not be present in the paste unless they are specifically provided as microscopic entrained air bubbles to provide durability in freeze-thaw environments. In real life, though, economics and local aggregate sources dictate the quality of materials used. The result is that excess voids often exist between the aggregate particles that must now be filled by paste and air. The challenge becomes producing an appropriate amount of the best possible quality paste, so that the resulting

hardened paste will fill the excess voids with durability and strength approaching that of the aggregates (Neville, 2005).

2.17.1 Contributions of Fly Ash to Concrete Durability and Strength

Durability and strength are not synonymous when talking about concrete. Durability is the ability to maintain integrity and strength over time. Strength is only a measure of the ability to sustain loads at a given point in time. Two concrete mixes with equal cylinder

Compressive strength at 28 days can vary widely in their permeability, resistance to chemical attack, resistance to cracking and general deterioration over time — all of which are important to durability.

Cement normally gains the great majority of its strength within 28 days, thus the reasoning behind specifications normally requiring determination of 28-day strengths as a standard. As lime from cement hydration becomes available (cements tend to vary widely in their reactivity), it reacts with fly ash. Typically, concrete made with fly ash will be slightly lower in strength than straight cement concrete up to 28 days, equal strength at 28 days, and substantially higher strength within a year's time. Conversely, in straight cement concrete, this lime would remain intact and over time it would be susceptible to the effects of weathering and loss of strength and durability (Swamy *et al.* 1986).

An extremely important aspect of the durability of concrete is its permeability. Fly ash concrete is less permeable because fly ash reduces the amount of water needed to produce a given slump, and through pozzolanic activity, creates more durable CSH as it fills capillaries and bleed water channels occupied by water-soluble lime (calcium

hydroxide). Fly ash improves corrosion protection. By decreasing concrete permeability, fly ash can reduce the

rate of ingress of water, corrosive chemicals and oxygen — thus protecting steel reinforcement from corrosion and its subsequent expansive result. Fly ash also increases sulfate resistance and reduces alkali-silica reactivity. At this point a distinction between Class C and Class F fly ashes needs to be made. While both improve the permeability and general durability of concrete, the chemistry of Class F ashes has proven to be more effective in mitigating sulfate and alkali-silica expansion and deterioration in concrete. Some Class C fly ashes have been used to mitigate these reactions, but must be used at higher rates of cement replacement. Fly Ash in concrete can reduce sulfate attack in two additional ways:

- Fly ash reduces calcium hydroxide, which combines with sulfates to produce gypsum. Gypsum is a material that has greater volume than the calcium hydroxide and sulfates that combine to form it, causing damaging expansion.
- Aluminates in the cement also combine with sulfates to form expansive compounds. By replacing cement, the amount of available aluminates is reduced, thereby lowering the potential for this type of expansive reaction.

In reducing alkali-silica reactivity, fly ash has the ability to react with the alkali hydroxides in Portland cement paste, making them unavailable for reaction with reactive silica in certain aggregates. Certain studies suggest that greater than 30% replacement with fly ash for cement has a dramatic effect in combating this expansive reaction.

2.17.2 Fly Ash and Heat of Hydration in Concrete

The hydration of cement is an exothermic reaction. Heat is generated very quickly, causing the concrete temperature to rise and accelerating the setting time and strength gain of the concrete. For most concrete installations, the heat generation is not detrimental to its long-term strength and durability. However, many applications exist where the rapid heat gain of cement increases the chances of thermal cracking, leading to reduced concrete strength and durability. In these applications, replacing large percentages of cement with fly ash (fly ash generates only 15 to 35 % as much heat as compared to cement at early ages) can reduce the damaging effects of thermal cracking. While the first structures to apply this concept in earnest were hydroelectric dams built in the 1930s and 1940s with 40% to 50% cement replacement, warm weather concreting and the risk of thermal cracking is a problem that exists today for all concrete. Warm weather will naturally raise the temperature of concrete aggregates, which make up the majority of the mass in concrete. This natural heating of the aggregates, coupled with solar heating at the construction site, can cause even thin concrete slabs to suffer the damaging effects of thermal cracking, along with finishing difficulties caused by rapid uncontrolled setting. Replacing 20% to 35% of the cement for "everyday" concrete in warm conditions will help reduce thermal cracking and provide the time needed to obtain the desired finish (Swamy *et al.* 1986).

2.17.3 Thermal Properties of Concrete

Coefficient of thermal expansion is defined as the change in unit length per degree of temperature change. Selecting an aggregate with a low coefficient of thermal expansion when it is economically feasible and technologically acceptable, may under certain conditions, become a critical factor for crack prevention in mass concrete. This

is because the thermal shrinkage strain is determined both by the magnitude of temperature drop and the linear coefficient of thermal expansion of concrete; the latter, in turn, is controlled primarily by the linear coefficient of thermal expansion of the aggregate which is the primary constituent of concrete.

The reported values of the linear coefficient of thermal expansion for saturated Portland cement pastes of varying water/cement ratios, for mortars containing 1:6 cement/natural silica sand, and for concrete mixtures of different aggregate types are approximately 18, 12, and 6 to 12 × 10−6 per °C, respectively. The coefficient of thermal expansion of commonly used rocks and minerals varies from about 5 × 10−6 per °C for limestones and gabbros to 11 to 12 × 10−6 per °C for sandstones, natural gravels, and quartzite. Since the coefficient of thermal expansion can be estimated from the weighted average of the components. The results are fairly close to the experimentally measured values of thermal coefficients reported in the published literature for concrete tested in moist condition, which is representative of the condition of typical mass concrete.

Specific heat is defined as the quantity of heat needed to raise the temperature of a unit mass of a material by one degree. The specific heat of normal weight concrete is not very much affected by the type of aggregate, temperature and other parameters. Typically the values of specific heat are in the range of 0.22 to 0.25 Btu/lb.F.

Thermal conductivity gives the flux transmitted through a unit area of a material under a unit temperature gradient. The thermal conductivity of concrete is influenced by the mineralogical characteristics of aggregate, and by the moisture content, density, and temperature of concrete. Typical values of thermal conductivity for concretes containing different aggregate types range between 23-25 25 Btu in/h.ft2.F

2.17.4 Concrete Permeability

A low permeability concrete generally possesses high strength and is resistant to the ingress of water and salt solutions. The reinforcing steel in concrete structures begins to corrode earlier and corrodes faster when the surrounding concrete is porous because chloride, oxygen, and moisture can more easily reach the steel. Measuring permeability helps detect durability problems and allows timely and cost-effective protection of the concrete structure Neville (2000).

2.17.5 Hardening of Calcium Hydroxide and Calcium Silicate Binders

Use of pozzolana as a partial replacement with cement in mortar can improve its ultimate strength and modify its microstructure due to the formation of additional calcium silicate hydrate (C-S-H) phases through pozzolanic reaction between the pozzolana and calcium hydroxide formed during the hydration of cement. This leads to a decrease in the content of the calcium hydroxide in comparison to that of the hydrated cement. Therefore, presence of the pozzolana influences the progress of the cement hydration and its compounds. In fact, hydration mechanism becomes much more complicated since cement hydration and pozzolanic reaction follow different reaction processes at different rates. Hydration of cement proceeds much faster than the pozzolanic reaction that becomes usually effective between 3-14 days of hydration, which is after most of the alite in the cement has hydrated. This period depends relatively on the reactivity and specific surface area of the pozzolana. Hydration of alite and belite has been reported to be accelerated with the presence of pozzolana. This can be explained by the fact that fine pozzolana grains act as a precipitation site for additional C-S-H phases and dissolution of alite and belite is accelerated as a result of the decrease in the Ca^{+2} ions concentration due to their consumption through

pozzolanic reaction. Literature concerning the hydration of cement in the presence of additional lime is rather limited. Hydration of tricalcium aluminate has been reported to be slightly retarded in the presence of lime. It has been found that hexagonal hydro-aluminates are formed with the hydration of tricalcium aluminate. In addition, formation of additional C-S-H by pozzolanic reaction has been reported to result in a pore size refinement effect leading to a decrease in the large pores and increase in the fine pores. Strength increase of the cement mortars blended with pozzolana is, therefore, correlated with the additional C-S-H formation and pore size refinement effect. Carbonation of the cement blended with pozzolana and lime is generally neglected in the literature Zivica (1999).

2.18 High Strength Concrete and High Performance Concrete

Compressive strength of concrete is the most important parameter to assess its quality. All other concretes with strength more than the specified one are referred as High Strength Concretes (HSC). With the advancements in technology, the demand of HSC increased in the construction industry but then came the new buzz word 'High Performance Concrete'. According to Aitcin (1990), HPC is nothing but HSC as high strength concrete not only gives high ultimate strength but performs better in many aspects like durability, abrasion resistance and sulphate attack etc. ACI defines HPC as "Concrete meeting special combinations of performance and uniformity requirements that cannot always be achieved routinely using conventional constituents and normal mixing, placing and curing practices". In fact, in HPC, the basic ingredients of normal concrete are proportioned in such a way so as to achieve efficiently the desired properties of strength and durability. A major criticism against the ACI definition of HPC is that durability of concrete is not mandatory; it is one of the options. The

misconception that high-strength will automatically lead to high-durability has probably resulted in many cases of cracking and premature deterioration of HPC structures, as reported in the published literature, Mehta *et al.* (2001). The reason lies in the mix proportions used to achieve very high-strength; for example, commercial high-strength concrete mixtures are often designed to obtain high compressive strength at 28-days and at times high early-strength values of the order of 25-40 MPa at 1-day, together with 150-200mm slump for ease of constructability. Typically, these mixtures are composed of a high cement content, viz 450-500 kg/m3 Portland or blended Portland cement containing a relatively small amount of silica fume and fly ash or slag, a low water/cement on the order of 0.3 (with the help of a super plasticizing admixture), and an air-entraining agent when it is necessary to protect the concrete from cycles of freezing and thawing. Field experience shows that the foregoing high strength concrete mixtures are prone to suffer early cracking from a variety of causes, such as a large thermal contraction due to the high Portland cement content, a large autogenous shrinkage due to the low water-cementitious ratio, and a high drying shrinkage due to the

high cement paste-aggregate ratio. Aitcin (1990) prefers to define HPC as a low water/binder concrete with an optimized aggregate-to-binder ratio to control its dimensional stability (i.e. drying shrinkage), and which receives an adequate water-curing (to control autogenous shrinkage). This definition adequately addresses the potential for lack of durability of HPC concrete except with massive structural members that may be subject to thermal cracking. In

this regard, an earlier definition proposed by Mehta *et al.* (1982) stated that the term HPC should be applied to concrete mixtures possessing the following three characteristics: high workability, high strength, and high durability.

2.18.1 Use of Fly Ash in High Performance Concrete

The use of fly ash in high performance concrete has been tried for long and sufficient literature and data is available on the topic but very little research has been done in India on this front. Moreover, the properties of fly ash available from various sources and even from same source at different times are not constant. Therefore, the results available on a particular fly ash in a particular country can not be fitted in every where. Hence, there is a scope of studying the effect of varying percentages of fly ash on various properties of different grades of concrete in India. Fly ash is most commonly used as a pozzolana in concrete. Pozzolanas are siliceous or siliceous and aluminous materials, which in a finely divided form and in presence of water, react with calcium hydroxide at ordinary temperatures to produce cementitious compounds. The spherical shape and particle size distribution of fly ash improves the fluidity of fill, thereby, reducing the demand of mixing water and contributing to long term strength of high strength concrete with fly ash. The use of fly ash in HSC and HPC has been studied by various researchers in past. The use of fly ash in concrete has been encouraged all over the world, Adams (1988). Naik *et al.* (1989) replaced 40% cement by fly ash and achieved an increase in strength of concrete of 23% and 38% at 28 days and 56 days, respectively. Raju *et al.* (1994) tried a 40% replacement of cement by fly ash and achieved a characteristic strength of 45 Mpa at 28 days with W/C ratio 0.4. The benefits of incorporating fly ash in to concrete have been demonstrated through extensive research and countless highway and bridge construction projects. Benefits to concrete vary depending on the type of fly ash, proportion used and other mix ingredients, mixing procedure, field conditions and placement. Some of the benefits of fly ash in concrete are (American Coal Ash Association (1995))

2.19 Pozzolana and Concrete Shrinkage

Shrinkage is the decrease of concrete volume with time. This decrease is due to change in moisture content of the concrete and physio-chemical changes, which occur without stress attributable to actions external to the concrete. Swelling is the increase of concrete volume with time. Shrinkage and Swelling are usually expressed as dimensionless strain (in/in. or mm/mm). Under given conditions of relative humidity and temperature, shrinkage is primarily a function of the paste, but is significantly influenced by the stiffness of the coarse aggregate. The interdependence of many factors creates difficulty in isolating causes and effectively predicting shrinkage without extensive testing

Shrinkage, expansion and creep are widely recognised as fundamental properties of concrete. It is therefore necessary to know exactly how pozzolanas can influence these parameters. In this respect, it should be remembered that a large percentage of cracks forming in the concrete structures is due to the restraints opposed to the shrinkage. It is generally assumed that drying shrinkage is not substantially influenced by pozzolanas in themselves. Variations, if any, should be ascribed to changes occurring in the water demand and in the microstructure of cement pastes. Shrinkage does not depend on the strength of the concrete: this is true either if the binder (cement +fly ash) content and the w/c ratio are constant or if the workability is kept constant by modifying the composition and thus the strengths. As a rule, shrinkage depends on the cement content and the w/c ratio. Variations with the same sign in both parameters make shrinkage increase or decrease, whereas variations having opposite signs contrast reciprocally.

During this period moisture may evaporate faster from the concrete surface than it is replaced by bleed water from layers of the concrete mass. Paste of rich mixes such

as high strength/performance concrete, will be more susceptible to plastic shrinkage than normal concrete. Autogenous shrinkage, due to self-desiccation, is perhaps more likely at very low water cement ratio. There is little data available for high strength concrete on autogenous shrinkage. Drying shrinkage occurs after the concrete has already attained its final set and a good portion of the chemical hydration process in the cement gel has been accomplished. Drying shrinkage of high strength concrete, although perhaps potentially larger due to higher paste volumes, do not, in fact appear to be appreciably large than normal strength concrete.

This is probably due to the increase in stiffness of stronger mixes.

Pozzolanic materials like silica fume Fly ash and typically increase the dry shrinkage due to several factors. With adequate curing pozzolans generally increase pore refinement. Use of a pozzolans results in an increase in the relative paste volume due to two mechanisms. Pozzolans have a lower specific gravity than Portland cement and in practice more slowly reacting pozzolans such as silica fume and Fly ash are frequently added in order to attain specified strength at 28 days. Additionally, pozzolans such as fly ash and silica fume do not contribute significantly to early age strength. Pastes containing pozzolans generally have a lower stiffness at earlier ages as well, making them more susceptible to increased shrinkage under standard testing conditions. Silica fume will contribute to strength at an earlier age than Fly ash but may still increase shrinkage due to pore refinement. Chemical admixtures tend to increase shrinkage. If they are used to reduce the evaporable water content of the mix, the shrinkage will be reduced. Air entraining agents, however, are found to have little effect on shrinkage. From the literature review it may be summed up that the mechanical properties of high strength concrete as the function of properties of the constituent of

the concrete. The durability and other properties of the high strength concrete increases with the use of the pozzolanic materials namely fly ash and silica fume.

2.20 Pozzolana and Fire Resistance in Concrete

The behaviour of structures exposed to fire is usually described in terms of the concept of fire resistance, which is the period of time under exposure to a standard fire time-temperature curve at which some prescribed form of limiting behaviour occurs. In performance-based design this limiting behaviour may be defined as real structural collapse or as a failure of integrity (which allows fire-spread to occur), but is more usually defined in terms of a deflection limit. Current design codes have taken a step towards full performance-based design by allowing designers to treat fire as one of the basic design limit states, taking account of:

- Non-uniform heating due to partial protection, which may be inherent in the framing system or specially applied,
- The level of loading in the fire limit state, using partial safety factors lower than those used for ultimate limit states, because of the relative improbability of such accidental conditions,
- Realistic stress-strain characteristics of materials at elevated temperatures.

The main limitation of these codified approaches is that they are based on the behaviour under test of isolated simply supported members, usually heated according to the standard ISO834 time-temperature curve3. In real buildings structural elements form part of a continuous assembly, and building fires often remain localised, with the fire-affected region of the structure receiving significant restraint from cooler areas

surrounding it. The real behaviour of these structural elements can therefore be very different from that indicated by standard furnace tests.

Evaluation on the behaviour of a material when exposed to fire is significant from the life safety point of view. The fire resistance test that was conducted on POFA reveals that this agro based aerated concrete able to perform excellently in every test that has been conducted. Although the material tested shows changes in colour from black to grayish but this material still able to exhibit good fire resistance. Not only that, it was discovered that inclusion POFA does not make the product to be combustible material or helps the spreading of fire. This present finding seems to be consistent with research conducted by some earlier researchers who highlighted that the replacement of Ordinary Portland cement by pozzolanic material improves fire resistance properties Khairunisa *et al.* (2010)

2.21 Creep

The deformation under load (creep) of concrete is an important time-dependent parameter involving structural mechanics inasmuch as creep influences the loss of pretension, the long-term deformation of structures and the load displacement from the concrete to the reinforcement. Factors affecting creep are various and can be distinguished as internal or external. Internal factors depend on the properties of concrete, while external ones are related to environmental conditions. In the first group the composition of concrete and therefore of the cement itself is found. Creep generally increases as the replacement for fly ash increases. Sometimes, however, the effect is more marked for small than for large replacements. Also in fly ash-containing concretes, creep increases as the strength decreases as well as load and time increase.

With regard to creep, the behaviour of blended cements is substantially different from that observed for the strength and shrinkage of concretes. Substitutions up to 50% for fly ashes cause minor variations in strength and shrinkage but modify creep heavily. Concretes with slightly different compositions designed to attain the same workability have shown that samples containing fly ashes had a specific creep approximately 50% higher than that found in fly-ash-free samples.

2.22 Effects of Natural Pozzolan on Concrete Properties

The most effective method for evaluating the performance of a concrete containing a natural pozzolan and establishing proper mixture proportions for a specific application is the use of trial batches and a testing program. Because some natural pozzolans perform better than others and project requirements differ, optimum proportions for a given combination of pozzolan and Portland cement cannot be predicted. When used as a replacement for a portion of portland cement, natural pozzolan replaces an equal volume or equal mass of the cement. Because the density of natural pozzolans is typically less than the density of portland cement, mass replacement results in a greater volume of total cementitious materials than when volume replacement is used at a given percentage. The mass of natural pozzolan employed may be greater than that of the replaced cement if the concrete is proportioned for optimum properties and maximum economy. Proportioning techniques for concrete including a finely divided mineral admixture are similar to those used in proportioning concrete that does not include such an admixture. Proportioning techniques for concrete mixtures are given in ACI 211.1. Specific procedures for proportioning mixtures containing pozzolans were developed by Lovewell and Hyland (1974). Finely divided mineral admixtures, whether natural pozzolan or other finely

divided material, should usually be regarded as part of the cement paste matrix in determining the optimum percentages of fine and coarse aggregate. The effect of the natural pozzolan on the mixing water requirement should also be determined. Some finely divided mineral admixtures cause a major increase in water requirement; others have little or no effect on water requirement, and still others typically reduce the water requirement of concrete in which they are used (Mather, 1958). Natural pozzolans affect the water requirement of the concrete and therefore the cement content. A natural pozzolan should be considered as part of the cementitious material (U.S. Bureau of Reclamation, 1975). The amount of natural pozzolan used varies significantly based upon the activity of the pozzolan.

Some natural pozzolans are used in a range of 15 to 35% based upon the mass of the total cementitious material in the concrete. More reactive natural pozzolans can be used in lower concentrations of 5 to 15% by mass of total cementitious material; however, such low concentrations may increase expansion resulting from the altered silica reaction in the presence of some alkali-reactive aggregates (Stanton, 1950). The optimal amount of natural pozzolan depends on where the concrete is used and the specifications for the work.

2.22.1 Effect of Pozzolan on Properties of Fresh Concrete

Natural pozzolans produce a cohesive mixture that maintains a plastic consistency, improving the workability. Typically, natural pozzolans absorb water from the mixture and hold this water in the system allowing for improved finishing. Where the available concrete aggregates are deficient in finer particle sizes, particularly material passing the 75 mm (No. 200) sieve, the use of a finely divided mineral admixture can reduce bleeding and segregation, and increase the strength of concrete by

supplying those fines missing from the aggregate (ACI 211.1). When an appropriate quantity of mineral admixture is used to correct such grading deficiencies, no increase in total water content of the concrete is required to achieve a given consistency or slump. Drying shrinkage and absorption of the hardened concrete are not greatly affected. A favourable particle shape, which is not flat or elongated, and a satisfactory fineness of the mineral admixture, however, are necessary qualities if a low water content is to be achieved without use of a water-reducing admixture. For example, coarse pozzolan of poor particle shape, such as finely divided pumicites, may require an increase in water content of the concrete for a given slump. This may contribute to increased bleeding and segregation of the fresh concrete. The use of finely divided mineral admixtures having pozzolanic properties can provide a major economic benefit in that the use of these materials permits a reduction in the amount of portland cement in the mixture. Although, aside from a reduction in water requirement, other technical benefits had not been spectacular. When the ratio of surface area of solids to volume of water is low, the rate of bleeding is relatively high. Moreover, most of the bleeding does not appear at the surface. The aggregate particles settle for a short period until they establish point-to-point contacts that prevent further settlement. The watery paste continues to bleed within the pockets defined by aggregate particles, leaving water-filled spaces at the undersides of the particles. Therefore, with such mixtures, bleeding tends to reduce homogeneity of the concrete. In extreme cases, the lack of homogeneity is manifested by open fissures large enough to be easily visible to the naked eye in a cross section of the concrete under the aggregate particles.

This lack of bond between paste and aggregate reduces the potential strength of concrete and increases permeability and absorption. These undesirable effects can be reduced by increasing the ratio of surface area of solids to volume of water in the paste.

This generally increases the stiffness of the paste and, at a given slump, effects a wider separation of the aggregate particles in the concrete. Increasing the amount of a suitable pozzolan usually increases the ratio of surface area of solids to volume of water. Natural pozzolans generally increase the cohesiveness of the mixture by producing a more plastic paste that allows the concrete to consolidate readily and flow freely under vibration. The increased cohesiveness also helps to reduce segregation. Natural pozzolans should have physical characteristics that allow the portland cement-pozzolan paste to contain a maximum proportion of solid matter and a minimum proportion of water. This requires that the mineral particles not have too high a surface area. The preferred shape would be a smooth, round particle instead of an irregular, rough-textured particle that would have a higher water demand. The high water demand of bentonite, which has a surface area considerably higher than cement, limits the use of that natural pozzolan to smaller percentages than those used in conventional concrete mixture proportions. As is the case with other pozzolans, for example, fly ash (ACI 232.2R), the use of natural pozzolan may extend the time of setting of the concrete if the portland cement content is reduced. The setting-time characteristics of concrete are influenced by ambient and concrete temperature; cement type, source, content, and fineness; water content of the paste; water soluble alkalies; use and dosages of other admixtures; the amount of pozzolan; and the fineness and chemical composition of the pozzolan. When these factors are given proper consideration in the concrete mixture proportioning, an acceptable time of setting can usually be obtained. The actual effect of a given natural pozzolan on time of setting may be determined by testing, when a precise determination is needed, or by observation, when a less precise determination is acceptable. Pressures on formwork may be increased when concrete containing a natural

pozzolan is used if increased workability, slower slump loss, or extended setting-time characteristics are encountered Mehta (2000).

2.23 Concrete Applications for Natural Pozzolans

Some manufacturers of concrete masonry units use as much as 35% pozzolan in the cementitious material for the manufacture of units cured using high-pressure steam. Others use from 15 to 35% in the cementitious material for the manufacture of units cured using low-pressure steam. Pozzolan reportedly gives added plasticity to the relatively harsh mixtures used in concrete masonry units (Belot, 1967). Autoclave curing is not as common as in the past, and some of the newer curing systems with short pre-set times can present early strength problems when some pozzolans of lower activity are used.

When natural pozzolan is used in concrete products cured in an autoclave at temperatures of 135 to 190 ^{0}C (275 to 374 F) and pressures of 0.5 to 1.2 MPa (75 to 170 psi), the cement content may be reduced by 30 to 35%. Particular care should be taken to ensure that the pozzolan meets the soundness requirement of ASTM C 618. The average cement replacement in low-pressure steam-curing applications is about 20% pozzolan. Tests for resistance to freezing and thawing of concrete masonry units containing pozzolans indicate that such units can be expected to perform well in vertical construction, such as walls. For the more severe conditions of horizontal exposure, a minimum compressive strength of 21 MPa (3045 psi) based on the net area of the unit is recommended when normal density aggregates are used. Air entrainment is not practical at the extremely low or zero slumps used for concrete masonry units. It could, however, be applicable to slump block or quarry tile. To provide adequate resistance to freezing and thawing for units made with concrete having appreciable slump, air entrainment is

needed (Redmond 1969). When proportioning mixtures, concrete product producers should check the grading and types of aggregates, cements, equipment, and curing temperatures, and then adjust trial batches with various amounts of pozzolans to achieve specific technical or economic objectives (Valore, 1970). Pozzolan can be used to reduce moisture absorption of masonry units.

2.23.1 Applications in Concrete pipes

Pozzolans may provide significant benefits in the manufacture of concrete pipes. Properly proportioned mixtures containing pozzolans lessen the permeability of concrete, and therefore, make pipe more resistant to weak acids and sulphates (Davis, 1954; Mather, 1982). The increase in sulphate resistance achieved depends on the type of cement, type of pozzolan, bedding and backfill used, groundwater, and sulphate concentration. Many concrete pipe producers use cement contents higher than needed for strength to obtain the required workability. Replacing some of the cement with pozzolan can reduce the cement content. In a packer-head pipe operation, concrete with a very dry consistency and low water content is compacted into a vertical pipe form using a revolving compaction tool. Equipment used in pipe production may last longer because of the lubrication effect. Use of a natural pozzolan can increase the cohesiveness of the no slump, freshly placed concrete, facilitating early form stripping. A reduction in the heat of hydration of concrete mixtures containing pozzolan can reduce the amount of hairline cracks on the inside surface of stored pipe sections (Cain, 1979) and concrete mixtures containing pozzolan tend to bleed less.

2.24 Other Uses of Natural Pozzolans

According to ACI 116R, grout is "a mixture of cementitious material and water, with or without aggregate, proportioned to produce a pourable consistency without segregation of the constituents." Its primary purpose is to fill spaces or voids. Mortar contains the same basic ingredients but with a less fluid consistency. It is used in masonry construction and is specified by ASTM C 270. This specification permits the use of natural pozzolans as blended cement. The effects of using natural pozzolans in mortars have not been fully investigated; however, they may affect bond strength, time of setting, and other important properties.

The benefits derived from using natural pozzolan in grouts are the same as for concrete, that is, economy, improved workability, lower heat of hydration, reduced alkali-silica reaction expansion, reduced permeability, and improved sulphate resistance. Common uses of grout include:

- In preplaced aggregate concrete, where grout is injected into the voids of previously placed coarse aggregate to produce concrete (ACI 304.1R);
- Contact grouting either under machinery to fill the space between a base plate and the substrate concrete or between the surface of concrete placed or pumped under existing concrete or rock, as in tunnel linings;
- To provide support for deep mine applications;
- In curtain grouting, where very fluid mixtures (often with the aggregate omitted) are used to fill cracks or fissures in rock;
- In soil and hazardous waste stabilization, to fill voids in the soil or between particles to decrease permeability, increase density, and generally improve its load-carrying capacity;

- In slab jacking, to raise and realign concrete slabs or structures that have settled; and
- In underwater placing and slope protection, where grout is generally injected into preplaced, inflatable cloth bags or blankets that are flexible enough to conform to the surrounding contour to fill the void and provide continuous contact.

2.24.1 Benefits and Advantages of the Natural Pozzolan

1. Lithification: Once the Natural pozzolan-lime mixture is hydrated, the pozzolanic reaction begins immediately and continues for many years. Eventually, the mass will reach complete lithification, forming a rocky material similar to plagioclase with some content of magnetite. The compressive strength as well as the flexural strength will continue to increase for a long time. This unique characteristic is one of the main reasons many great ancient structures have lasted for over two thousand years.
2. Autogenous Healing: A unique characteristic of Natural pozzolan is its inherent ability to actually heal or re-cement cracks within the concrete by means of the continuation of pozzolanic reaction with the calcium hydroxide freed from the cement hydration reaction. This results in the filling up of most of the gaps inside the hardened concrete matrix

3. Reduced Permeability and Voids: The leaching of water-soluble calcium hydroxide produced by the hydration of Portland cement can be a significant contributor to the formation of voids. The amount of "water of convenience" used to make the concrete workable during the placing process creates permeable voids in the hardened mass. Natural pozzolan can increase the

fluidity of concrete without "water of convenience," so that the size and number of capillary pores created by the use of too much water can be minimized.

4. Reduces Expansion and Heat of Hydration: Experiments show that replacing 30% Portland cement with Natural pozzolan can reduce the expansion and heat of hydration to as low as 40% of normal. This may be because there is no heat produced when Natural pozzolan reacts with calcium hydroxide and that the free calcium oxide in the cement can hydrate with natural pozzolan to form C-S-H. Natural pozzolan decreases the heat generated by cement hydration and delays the time of peak temperature. The graphic pattern of Natural pozzolan - Portland cement mixture is extended longer and lower to form a much more moderate curve than the heat of hydration curve of Portland cement itself Mehta, P.H(2000)

5. Reduces Creep and Cracks: While concrete is hardening, the "water of convenience" dries away. The surface of the hardening mass then begins to shrink as the temperature goes down from outside. This results in the formation of creep and cracks. Natural pozzolan moderates the expansion and shrinkage of concrete. It also helps to lower the water content of the fresh concrete. Therefore, the creep and cracks can be significantly reduced without the process of water cooling.

6. **Reduces Micro-cracking**: The expansion and shrinkage mentioned above also create micro-cracks inside the hardened C-S-H paste and in-between the aggregate and the C-S-H paste. These micro-cracks significantly contribute to concrete permeability as well as other concrete defects. The Natural pozzolan-

Portland cement mixture expands these shrinks so moderately that there is no micro-cracking inside the C-S-H paste after drying Tay *et al.* (1991).

7. **Increases Compressive Strength**: The pozzolanic reaction between natural pozzolan and calcium hydroxide happens after the C3S and C2S in the cement begins to hydrate. At the early stage of curing, 30% Natural pozzolan substituting Portland cement mixture is slightly lower than reference OPC [Ordinary Portland Cement} in regard to compressive strength. As time goes by, natural pozzolan continues to react with the calcium hydroxide produced by cement hydration and increases the compressive strength by producing additional C-S-H. After 21 curing days, the 30% Natural pozzolan/ 70% Portland cement mixture begins to exceed reference OPC in compressive strength. After 28 days, it exceeds reference OPC by about 15%. The pozzolanic reaction continues until there is no free calcium hydroxide available in the mass and the compressive strength exceeds the reference OPC by 30-40%.
8. **Increases Resistance to chloride Attack**: Concrete deterioration caused by the penetration of chloride occurs quickly when chloride ions react with calcium. The expansion of hydrated calcium oxy-chloride enlarges the micro-cracks and increases the permeability that causes quicker chloride penetration and more damage from freezing and thawing action. The 30% Natural pozzolan added into cement can react with almost all the free calcium hydroxide and form a much denser past. Thus, the penetration of chloride can be minimized and the few penetrated chloride ions cannot find free calcium hydroxide with which to react.

9. Increases resistance to sulphate attack: There are three chemical reactions involved in sulphate attack on concrete: 1) Combination of free calcium hydroxide and sulphate to form gypsum (CaSO4-2H2O). 2) Combination of gypsum and calcium aluminate hydrate (C-A-H) to form ettringite (C3A-3CaSO-32H2O). 3) Combination of gypsum and calcium carbonate with C-S-H to form thaumasite (CaCO3-CaSiO3-CaSO4-15H2O). All these reactions result in the expansion and disruption of concrete. Thaumasite in particular is accompanied by a very severe damaging effect which is able to transform hardened concrete into a pulpy mass.

10. **Reduces alkali-aggregate reaction**: Because Natural pozzolan is shattered into such a fine particle size resulting in dramatically increased reactive surface area, it can react quickly with calcium hydroxide and can trap the alkali inside the cement paste. Thus, it helps to form a denser paste with almost no alkali aggregate reaction at all.

11. **Protects steel reinforcement from corrosion**: The preceding discussions make it very clear that concrete made from 30% Natural pozzolan/ 70% Portland cement mixture can protect steel reinforcement because it creates an environment so densely packed that no liquids or gases can penetrate through it to cause corrosion to the steel.

12. **Increases abrasion resistance**: Natural pozzolan increases the compressive strength of concrete and makes the concrete matrix stronger and more dense. It also prevents the formation of pulpy, crispy, or water-soluble materials created by chemical attack. Therefore, it helps the concrete to durably resist abrasion.

13. **Lowers water requirement**: with high fluidity, self-levelling, and compression: In normal operations, the bulk volume of concrete in the constructions are placed and compacted by use of high frequency poke vibrators. The rapid vibration induces segregation phenomena of all orders of magnitude in the fresh concrete, e.g., stone segregation, internal bleeding giving bonding failures, and inhomogeneous cement paste and air-void systems. Under proper use of vibratory compaction, Natural Pozzolan minimizes or eliminates these problems due to the amorphous structure of the pozzolan particles.

2.25.1 Curing Materials

The industry has moved away from moist curing toward the use of curing compounds that are more convenient to use. However, the use of high cement content, silica fumes, and low w/c ratio has made the concrete more prone to shrinkage and thermal cracking. Curing compounds are not effective in preventing shrinkage or cracking. New curing compounds are needed not only to prevent evaporation, but also to replenish lost mixture water. For example, the curing compound might include chemicals that could condense ambient moisture on the concrete surface to provide needed moisture.

2.25.2 Tests for Concrete

Tests for plastic concrete properties such as slump, air content, and unit weight have been useful in controlling the quality and consistency of concrete mixtures. However, it can be expected that stronger emphasis will be placed on shorter construction times on the nation's roads, bridges, and airports. The present tests for

plastic concrete tend to cause delays in construction. New technology is needed to enable testing of the workability, air content, and unit weight of mixtures in a nonintrusive manner. For example, a nonintrusive device similar to a radar gun could be developed for measuring the concrete workability from the concrete stream during discharge.

2.25.3 Tests for Hardened Concrete

A better means of predicting the strength and durability of concrete is needed. Tests based on the hydration process, rate of heat development, and other physical and chemical indicators should be developed for predicting the ultimate strength and durability of concrete. The availability of such tests would allow better optimization of the concrete mixture with respect to the types and proportions of its ingredients.

In addition, the concept of 28-day strength may become obsolete as an acceptance requirement. Concrete mixtures of the future may reach their ultimate strength in less than 7 days. This accelerated development of strength may alter the microstructure of the concrete.

Research is needed to better understand the physical and chemical properties of hydration products, as well as the extent of micro-cracking and volume change in the paste matrix.

Advances have been made in measuring the permeability of concrete to better predict its durability. Nonetheless, existing devices either are too slow or provide an indirect measure

of concrete permeability. Thus a fast, accurate, and repeatable device for determining the permeability of concrete is needed. A procedure should also be developed for predicting the durability of concrete from analysis of permeability data.

2.25.4 Technology Transfer

Good-quality research in concrete and its materials is being conducted. This research is generating new information and technologies. However, effective means of transferring the research findings and products from the research phase to application are needed. Many practitioners do not attend conferences, workshops, or meetings. These practitioners often do not receive full information on the properties of new materials and how these materials, individually or collectively, affect the strength, durability, and volume change of the concrete. A detailed plan for transferring the knowledge and new products resulting from completed research in concrete and its materials should be developed and implemented. The

Internet should be the centre piece of this plan.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Preamble

This chapter explains the materials used and the test carried out in conducting various experimental investigations. The materials used in the experimentation include coarse aggregate, fine aggregate, cement water and Corn Cob Ash. The manufacture and the test for evaluating the properties of Corn Cob Ash (CCA) modified cement and concrete specimens are also experimented. The preparation of the test specimens and the standards followed in conducting various durability performances of cement and concrete are carefully presented.

3.2 Coarse Aggregate (Flakiness and Elongation Test)

Coarse aggregate used for the experiment, comprised of crushed granite obtained from a quarry along km 15, Zaria – Kaduna road in Zaria. The Flakiness and elongation Index were determined by the method described in B.S. 812. Results for flakeness index, elongation index and are presented in tables 3.1 and 3.2 below.

Table 3.1: Result for Flakeness Index Test on Coarse Aggregates

Sieve sizes (mm)	Weight of 200 pieces (g)	Weight passing (g)
50.00	-	-
38.10	-	-
25.40	9.40	1.3
19.05	3.20	0.56
12.70	1.25	0.14
9.52	0.45	0.04
6.50	0.23	0.02
	∑=14.53	∑=2.06

Flakiness index = Total weight passing / Weight of 200 pieces x 100 = 14.18%.

Table 3.2: Result for Elongation Index Test on Coarse Aggregates

Sieve sizes (mm)	Weight of 200 pieces (g)	Weight passing (g)
50.00	-	-
38.10	-	-
25.40	9.40	7.31
19.05	3.20	2.76
12.70	1.25	0.5
9.52	0.45	0.27
6.50	0.23	0.12
	∑=14.53	∑=10.96

Elongation index = Total weight passing / Weight of 200 pieces x 100 = 24.57%.

3.2.1 Coarse Aggregate (Particle Size Distribution)

Samples of coarse aggregate were prepared in accordance with the procedures described in BS 812-102:1984 and sieve analysis was carried out. The results are presented in the table 3.3 below.

Table 3.3: Sieve Analysis of Coarse Aggregate

Sieve size (mm)	% Weight passing
20	-
12.5	77.5
10.0	38.5
6.3	0.9
2.36	0.6
1.18	0.5
600µm	

3.3 Fine Aggregate (Particle Size Distribution)

Fine aggregate used consisted of naturally occurring sand obtained from river Rafin Yashi in Zaria. The sieve analysis of the fine aggregate was carried out in accordance with B.S. 812 (1975). The result for the sieve analysis is presented in table 3.4 below.

Table 3.4: Sieve Analysis of Fine Aggregate

Sieve size (mm)	% Weight passing
10.0	100
5.0	98.0
2.36	70.8
1.18	35.2
600µm	17.8
300µm	10.2
150µm	5.0
75µm	

3.4 Cement (Consistency, Setting Time and Soundness Tests):

Dangote brand of Ordinary Portland cement was selected for use in this experiment. Physical and chemical tests have been carried out on the cement in accordance to BS EN 197-1(2000) test for cement. The results for the consistency test are presented in the table 3.5 below.

. Soundness of cement was determined by Le-Chatelier method as per BS EN 197-1(2000). The results for the test on the soundness and setting times of cement are presented in the table 3.6 below.

Table 3.5: Consistency Test on Cement

Sample Identification Mark	Consistency
A	30
B	30
C	30

Where A, B, C are sample identification marks. Three tests per sample were used.

Table 3.6: Results of setting time and soundness of cement

Sample Identification Marks	Initial Setting Time (min)	Final Setting Time (min)	Soundness (mm)
A	45	85	0.25
B	48	92	0.5
C	45	90	0.5

3.4.1 Cement (Fineness Tests):

. The method used to determine fineness of cement was AASHTO T 128: Fineness of Hydraulic Cement by the 75-mm (No. 200) Sieves. The fineness of cement was determined by sieving through 75μm sieve. Three separate samples of were weighed, sieved and the mass retained on the sieve was computed as a percentage of the total mass. These results are represented in table 3.7 below

Table 3.7: Results for fineness of cement

FINENESS TEST FOR CEMENT		
Wt. of Sample (g)	Mass Retained (g)	Fineness
50	1.5	0.03
60	2.5	0.04
70	3	0.04
	Fineness Value =	0.04

3.5 Water:

Water used for mixing and curing concrete was clean, fresh water from an approved source (tap water from the Civil Engineering Department. A. B. U. Zaria) and it was good for drinking i.e. portable.

3.6 Chemical Composition of Corn Cob Ash

Corn Cobs used for this research were collected from Shika, Giwa and Zango villages around Zaria, in Kaduna State of Nigeria. Corn Cob Ash was obtained from the

Ash of burned Corn cobs. The cobs were burned in an open incinerator in open air. The ash resulting from the combustion was used in the experiment.

The Corn Cob ash was analyzed using an energy dispersive x-ray fluorescence (EDXRF) machine to determine the elemental and oxide composition of the ash. The analysis was carried out at Center for Energy Research in Zaria. The oxide composition is presented in the table 3.8 below.

Table 3.8: Chemical composition of Corn Cob Ash

CONSTITUENTS	PERCENTAGE COMPOSITION
Aluminum Oxide (Al_2O_3)	18.30
Silicon dioxide (SiO_2)	61.50
Potassium Oxide (K_2O_3)	2.55
Calcium Oxide (CaO)	3.02
Manganese Oxide (Mn_2O_3)	1.71
Iron Oxide (Fe_2O_3)	8.66
Copper Oxide (CuO)	0.27
Titanium Oxide (TiO_2)	0.53
Potassium Oxide (K_2O_3)	2.55
LOI	4.58

3.7 Corn Cob Ash Cement Test

The fundamental tests for cement quality are those for setting time, soundness, strength and fineness. These tests were carried out according to BS EN 197-1:2000 but with cement/ CCA ratios of 90:10, 80:20, 70; 30, and 60:40 in that order. The CCA was

mixed with cement to form a binding media and resulting mix was subject to test as though they were cement.

3.7.1 Consistency of Cement / Corn Cob Ash Mix

The CCA / Cement samples were labeled D, E, F, G, and H. where D was the control sample containing 100% cement content and E, F, G, and H represent 10%, 20%, 30%, and 40% CCA/ Cement substitution. The cement type used was Dangote Brand of Ordinary Portland Cement. The test was carried in accordance with BS EN 197 P1 2000. The results for consistency are presented in table 3.9 of below.

Table 3.9: Consistency of cement partially replaced with different percentages of CCA

CONSISTENCY TEST	
Wt of cement (g)	Consistency
D	30.00
E	33.75
F	35.00
G	36.25
H	37.50

3.7.2 Soundness of Cement / CCA Mix

The 'Le Chatelier' test was used as a test for soundness in this study. The test is described under British practice under BS EN 197-1:2000. The samples were prepared in accordance BS EN 197-1:2000 for testing cement. A summary of the results obtained are presented in the table 3.10 below. The Cement /CCA samples were labeled D, E, F. G. and H. where D was the control sample with hundred percent cement content and E, F, G and H represent 10%, 20%, 30% and 40% CCA/ Cement substitution.

Table 3.10: Soundness of cement / CCA mix

SOUNDNESS TEST		Code Specification
Cement / CCA Substitution	Average Expansion (mm)	BS 4550, NIS 447
D	1.5	$\leq$ 10 mm
E	1.5	
F	1.0	
G	0.5	
H	0.5	

3.7.3 Setting Times of Cement/ CCA Mix

A similar mixture of cement/ CCA pastes was prepared to determine the setting time. The experiment carried out to determine the setting times for a cement/ CCA sample were prepared in accordance with BS EN 197-1:2000 for testing cement,. A summary of the results obtained are presented in the table 3.11 below.

Table 3.11: Setting times of cement partially replaced with different percentages CCA

Sample Identification Marks	Initial Setting Time (min)	Final Setting Time (min)	Soundness (mm)
D	45	85	0.25
E	48	100	0.5
F	54	130	0.5
G	93	172	0.75
H	116	227	0.25

3.8 Compressive Strength of Cement CCA/Ash Concrete

Concrete cubes samples containing CCA as cement replacement by mass were prepared. Concrete cubes were designed to meet an expected strength of 30 N/mm^2 with a slump of 50mm. the water / cement ratio was 0.5 (See summary of absolute mix design in appendix 1 and 2). In this experiment, OPC/ CCA ratio of 100:0, 90:10, 80:20, 70:30, 60:40 and 50:50 were made.by weight and were labeled M1, M2, M3,

M4, M5 and M6. M1 is therefore the control sample. Three sample cubes each with dimension 150mm x 150mm x 150mm were prepared for the experiment. The concrete materials cement, aggregates and ash were mixed by hand. The materials were mixed together thoroughly by stirring to form a uniform mass. The moulds were cleaned with engine oil to prevent bond between the mould and the concrete and permit easy stripping. The workability of each of the mixes was determined using slump test according to BS 1881; Part 102 (1983). The freshly mixed concrete was scooped into the mould. Each mould was filled in three layers with the concrete; each layer was tamped 25 times with a tamping rod. Cubes were cast using metal moulds (150mm×150mm) and compaction was done manually. The concrete cubes in the moulds were left in the laboratory for 24 hours. Stripping of the concrete cubes from the mould was carefully done after 24 hours of casting.

These samples were used for the compression tests. The specimens were cured in curing tank containing clean water at a temperature of 18°C to 22°C in a curing room at the concrete laboratory at Ahmadu Bello University, Zaria. The cubes were crushed to determine their compressive strength at ages 1, 3, 7 and 28 days in accordance with BS 1881, Part 116 (1983). Also measured was the density of the specimens the total number of cubes casted was seventy two.

The weight of experimental materials is shown in the table in the appendix 2. Table 3.12 to 3.16 presents the average compressive strengths of specimens modified with CCA and Table 3.17 presents the variation in density of cube specimens as age increases.

Table 3.12: Compressive Strength of Specimens prepared with 10% percent of CCA as cement replacement.

Cube Identification marks	Age for testing (days)	Crushing strength (N/mm^2)
M2(1)	1	5.56
M2(3)	3	8.67
M2(7)	7	21.11
M2(28)	28	29.56

Each value is an average of 3 samples. M2 (1) is concrete mix type 2 tested at day 1, M2 (3) is concrete mix type 2 tested at day 3, M2 (7) is concrete mix type 2 tested at day 7 and M2 (28) is concrete mix type 2 tested at day 28

Table 3.13: Compressive Strength of Specimens prepared with 20% percent of CCA as cement replacement.

Cube Identification marks	Age for testing (days)	Crushing strength (N/mm^2)
M3(1)	1	4.89
M3(3)	3	8.44
M3(7)	7	13.78
M3(28)	28	20.67

Each value is an average of 3 samples. M3 (1) is concrete mix type 3 tested at day 1, M3 (3) is concrete mix type 3 tested at day 3, M3 (7) is concrete mix type 3 tested at day 7 and M3 (28) is concrete mix type 3 tested at day 28

Table 3.14: Compressive Strength of Specimens prepared with 30% percent of CCA as cement replacement.

Cube Identification marks	Age for testing (days)	Crushing strength (N/mm^2)
M4(1)	1	3.11
M4(3)	3	7.78
M4(7)	7	11.78
M4(28)	28	15.56

Each value is an average of 3 samples. M4 (1) is concrete mix type 4 tested at day 1, M4 (3) is concrete mix type 4 tested at day 3, M4 (7) is concrete mix type 4 tested at day 7 and M4 (28) is concrete mix type 4 tested at day 28

Table 3.15: Compressive Strength of Specimens prepared with 40% percent of CCA as cement replacement.

Cube Identification marks	Age for testing (days)	Crushing strength (N/mm^2)
M5(1)	1	2.89
M5(3)	3	5.56
M5(7)	7	11.33
M5(28)	28	13.78

Each value is an average of 3 samples. M5 (1) is concrete mix type 5 tested at day 1, M5 (3) is concrete mix type 5 tested at day 3, M5 (7) is concrete mix type 5 tested at day 7 and M5 (28) is concrete mix type 5 tested at day 28

Table 3.16: Compressive Strength of Specimens prepared with 50% percent of CCA as cement replacement.

Cube Identification marks	Age for testing (days)	Crushing strength (N/mm^2)
M6(1)	1	2.22
M6(3)	3	4.22
M6(7)	7	10.44
M6(28)	28	13.78

Each value is an average of 3 samples. M6 (1) is concrete mix type 6 tested at day 1, M6 (3) is concrete mix type 6 tested at day 3, M6 (7) is concrete mix type 6 tested at day 7 and M6 (28) is concrete mix type 6 tested at day 28

Table 3.17 variation in density of Concrete cubes with CCA as partial cement replacements.

Identification marks	Average Density of cubes kg/m^3			
	1 day	3days	7 days	28 days
M1	2400.00	2400.00	2370.37	2370.37
M2	2400.00	2370.37	2370.37	2370.37
M3	2370.37	2370.37	2311.11	2311.11
M4	2311.11	2311.11	2281.48	2251.85
M5	2311.11	2311.11	2251.85	2281.48
M6	2281.48	2251.85	2281.48	2281.48

3.9 Durability Studies:

Aggressive solutions used in these experiments were classified into inorganic acids, organic acids and salt solutions. In this vain, Sulphuric acid solution, acetic acid solution and magnesium sulphate solution were selected for the experiments. Concentrations of 5% and 10% of each of the solutions were used for the experiments. Properties of each of these acids are summarized in sections 10a, 10b, and 10c below. The cubes were prepared in the same manner as in section 3.9 and were soaked in various concentrations of acids. The concentration of the solutions was controlled by periodically renewing the strength of solutions every four weeks throughout the immersion period.

In this investigation, concrete cube specimens were first cured in water for 28 days before putting them into 5 % and 10% acid solutions of, Sulphuric acid, acetic acid, and sodium sulphate. Concrete cube specimens that have been put into solution were periodically subjected to visual inspection. The durability performance of OPC and CCA/ OPC concrete specimens were then determined by periodic measurement of weight losses of the samples continuously immersed in the test solution. . Mass change measurements were done after every two weeks (336 hours). Before each reading the specimens were carefully brushed and cleaned with water to remove salt from the surface. Prior to weighing, the specimens were cleaned with a dry rag to bring the surface to a dry condition.

At the end of the curing period, the concrete cube specimens were subjected to compression for assessing residual strength. These tests were performed at 60days and 90days after soaking in acid solutions. For each set of samples, a control specimen was prepared containing only OPC cement. These control specimens were labeled M1 in the experiment. The other set of specimens labeled M2, M3, M4, M5 and M6 had CCA/ Cement proportions of 10%, 20%, 30%, 40% and 50%. Each set of specimens were soaked in acid

and their compressive strengths compared at the end of the curing period. The total number of specimen casted was two hundred and eighty eight.

a) Sulfuric acid

Sulfuric acid (Sulphuric acid in British English) is a strong mineral acid with the molecular formula H_2SO_4. It is soluble in water at all concentrations. The properties are shown in table 3.18 below

Table 3.18: Properties of Sulphuric acid

Molecular formula	H_2SO_4,
Molar mass	98.08 g mol−1
Appearance Clear	Colorless, odorless liquid
Density	1.84 g/cm^3
liquid Melting point	10 °C, (283 K), (50 °F)
Boiling point	337 °C, (610 K), (639 °F)
Solubility	Miscible.in water
Acidity (pK_a)	4.76 at 25 °C
Viscosity	26.7 Pa·s (20 °C)

b) Sodium sulfate

Sodium sulfate is the sodium salt of sulfuric acid. It is a white crystalline solid of formula Na_2SO_4 known as the mineral thenardite. Properties are shown in table 3.19 below.

Table 3.19: Properties of Sodium Sulphate

Molecular formula	Na_2SO_4,
Molar mass	142.04 g/mol
Appearance	white crystalline solid hygroscopic
Density	2.664 g/cm3 (anhydrous)
Melting point	884 °C (anhydrous)
Boiling point	1429 °C (anhydrous),
Solubility in water	4.76 g/100 ml (0 °C). 42.7 g/100 ml (100 °C)

c) Acetic Acid

Acetic Acid, (common name of ethanoic acid), CH_3COOH, a colorless liquid with a sharp, irritating odor and sour taste. In aqueous solution, it functions as a weak acid. Properties are shown in tables 3.20 below.

Table 3.20: Properties of Acetic Acid.

Molecular formula	$C_2H_4O_2$,
Molar mass	60.05 g mol^{-1}
Appearance	Colorless liquid
Density	1.049 g/cm^3 (l), 1.266 g/cm^3 (s)
Melting point	16.5 °C, (290 K),(62 °F)
Boiling point	118.1 °C, (391 K),(245 °F)
Solubility	Miscible in water
Acidity (pKa)	4.76 at 25 °C
Viscosity	1.22 mPa•s at 25 °C

3.10 Visual Inspection

Visual inspection of concrete test specimens attacked by acid revealed that the acids dissolve the paste that holds the aggregate in place. Acid attack in this research was diagnosed primarily by surface dissolving of CCA/ Cement paste exposing aggregates on the specimens. Photographs showing extent of dissolving are presented in plates 1 to 36 in the appendix 3 and discussed in chapter four.

3.11 Loss of Weight

The details on loss of weight of concrete cube specimens at different periods of exposure up to 60 days (1440 hour) in different acid solutions were measured to determine the extent of deterioration. Control specimens were also prepared for comparison. Tables 3.21 to 3.26 shows the loss in weight of cube test specimens soaked in different Solutions after 60 days and 90 days.

Table 3.21: Loss of weight of CCA/cement concrete in 5% and 10 % concentrations of tetraoxosulphate VI acid solutions after 60 days

Identification Mark	10% H_2SO_4 Solution (60 days) (kg)	5% H_2SO_4 Solution (60 days) (kg)
M1	0.2	0.3
M2	0	0.4
M3	0.1	0.1
M4	0.1	0.1
M5	0	0
M6	0.4	0.2

Table 3.22: Loss of weight of CCA/cement concrete in 5% and 10 % concentrations of tetraoxosulphate VI acid solutions after 90 days

Identification Mark	10% H_2SO_4 Solution (90 days) (kg)	5% H_2SO_4 Solution (90 days) (kg)
M1	0.2	0.1
M2	0	0.1
M3	0.1	0.1
M4	0.1	0.1
M5	0.2	0.1
M6	0.3	0.2

Table 3.23: Loss of weight of CCA/ Cement concrete in 5% and 10 % concentrations of Acetic acid solutions after 60 Days

Identification Mark	10% Acetic acid Solution (60 Days) (kg)	5% Acetic acid Solution (60 Days) (kg)
M1	0.3	0.3
M2	0.2	0.2
M3	0.1	0.4
M4	0.2	0.1
M5	0.3	0.1
M6	0.1	0.1

Table 3.24: Loss of weight of CCA/ Cement concrete in 5% and 10 % concentrations of Acetic acid solutions after 90 Days

Identification Mark	10% Acetic acid Solution (90 Days) (kg)	5% Acetic acid Solution (90 Days) (kg)
M1	0.2	0.2
M2	0.1	0.1
M3	0.2	0.1
M4	0.1	0.1
M5	0.2	0.2
M6	0.3	0.2

Table 3.25: Loss of weight of CCA/ Cement concrete in 5% and 10 % concentrations of Sodium Sulphate solutions after 60 Days.

Identification Mark	10% Acetic acid Solution (60 Days) (kg)	5% Acetic acid Solution (60 Days) (kg)
M1	0	0.1
M2	0.4	0.3
M3	0.2	0.2
M4	0.4	0.3
M5	0.2	0
M6	0.2	0.3

Table 3.26: Loss of weight of CCA/ Cement concrete in 5% and 10 % concentrations of Sodium Sulphate solutions after 90 Days.

Identification Mark	10% Acetic acid Solution (90 Days) (kg)	5% Acetic acid Solution (90 Days) (kg)
M1	0.2	0.3
M2	0.1	0.1
M3	0.2	0.1
M4	0.2	0.2
M5	0.2	0.1
M6	0.2	0.2

3.12 Density of Cubes

The effect of the different aggressive media on the test specimens was also investigated with respect to density. The results are presented in the table 3.27 below.

Table 3.27: Average Density cubes with varying CCA/ Cement percentage replacement and varying age

Identification Mark	Average Density of cubes kg/m^3			
	1 day	3days	7 days	28 days
M1D	2400.00	2400.00	2370.37	2370.37
M2D	2400.00	2370.37	2370.37	2370.37
M3D	2370.37	2370.37	2311.11	2311.11
M4D	2311.11	2311.11	2281.48	2251.85
M5D	2311.11	2311.11	2251.85	2281.48
M4D	2281.48	2251.85	2281.48	2281.48

3.13 Compressive Strength Test

Cube specimens were cured in different acidic environments. Compressive strength of Corn Cob Ash / OPC concrete at 60 & 90 days in different acidic

environment are measured. The cube strength obtained was then compared with standards and between test results. Results of compressive strength for specimens soaked in 5% and 10% of different acidic media are for 60 days and 90 days are presented in tables 3.28 to 3.34.

Table 3.28: Average Compressive strength of test samples in 5% concentration of Sulphuric acid solution after 60 and 90 days.

	Age/ Days	Average Compressive Strength of Concrete N/mm^2					
		M1S	M2S	M3S	M4S	M5S	M6S
5% H_2SO_4	60	31.25	24.89	21.52	15.57	14.1	10.7
	90	33.78	28.56	21.25	16.89	14.1	11.56

Table 3.29: Average Compressive strength of test samples in 10% concentration of Sulphuric acid solution after 60 and 90 days.

	Age/ Days	Average Compressive Strength of Concrete N/mm^2					
		M1S	M2S	M3S	M4S	M5S	M6S
10% H_2SO_4	60	33.78	29.11	21.62	14.22	11.56	10.7
	90	37.33	28.44	19.57	19.56	13.33	10.67

Table 3.30: Average Compressive strength of test samples in 5% concentration of Sodium Sulphate solution after 60 and 90 days.

	Age/ Days	Average Compressive Strength of Concrete N/mm^2					
		M1S	M2S	M3S	M4S	M5S	M6S
5% Na_2SO_4	60	35.56	33.78	19.58	17.78	16.15	13.33
	90	39.11	30.22	21.56	19.56	13.33	13.33

Table 3.31: Average Compressive strength of test samples in 10% concentration of Sodium Sulphate solution after 60 and 90 days.

	Age/ Days	Average Compressive Strength of Concrete N/mm^2					
		M1S	M2S	M3S	M4S	M5S	M6S
10% Na_2SO_4	60	37.33	28.44	19.58	15.57	14.5	12.54
	90	39.11	29.33	21.25	15.11	13.33	13.25

Table 3.32: Average Compressive strength of test samples in 5% concentration of Acetic Acid solution after 60 and 90 days.

	Age/ Days	Average Compressive Strength of Concrete N/mm^2					
		M1S	M2S	M3S	M4S	M5S	M6S
5% CH_3COOH	60	33.78	24.89	21.52	15.11	12.15	12.7
	90	35.56	29.33	22.1	14.22	11.56	11.56

Table 3.33: Average Compressive strength of test samples in 10% concentration of Acetic Acid solution after 60 and 90 days.

	Age/ Days	Average Compressive Strength of Concrete N/mm^2					
		M1S	M2S	M3S	M4S	M5S	M6S
10% CH_3COOH	60	39.11	27.56	21.63	15.11	14.5	11.56
	90	41.78	29.78	21.52	13.33	13.3	11.11

Table 3.34: Average Compressive strength of test samples cured in water after 60 and 90 days.

	Age/ Days	Average Compressive Strength of Concrete N/mm^2					
		M1S	M2S	M3S	M4S	M5S	M6S
10% CH_3COOH	60	35.56	31.00	24.35	21.00	18.62	14.14
	90	40.50	34.35	27.25	24.10	20.15	15.17

CHAPTER FOUR

ANALYSIS AND DISCUSSION OF RESULTS

4.1 Preamble

The results of experiments carried out in chapter three are discussed in this chapter to arrive at reasonable conclusions. First the experiments on the properties of materials used are discussed. Next the experiments on the effects of Corn Cob Ash (CCA) used as a partial replacement of cement in mortars are discussed. Lastly the effect of different aggressive environment on concrete made from CCA and cement is discussed.

All of these experiments have been carried out in the heavy structural laboratory, department of Civil Engineering Ahmadu Bello University Zaria. The results are presented in Chapter three and analysed and discussed in this chapter.

4.2 Coarse Aggregate:

Tests carried out on this material includes flakiness index, elongation index and particle size distribution. The results are presented in tables 3.1, 3.2, and 3.3 in chapter three. The flakiness and elongation index measured in accordance to BS 812 Part 105 (1989) are 14.18 % and 24.57% respectively. These values are less than 30% as specified in the code. Therefore aggregates used in the experiments are free from flaky and elongated particles. The plot of the particle size distribution in figure 4.1 below showed that it is within Grading Zone 1 of B.S. 882 (1973). It also shows that it is well graded.

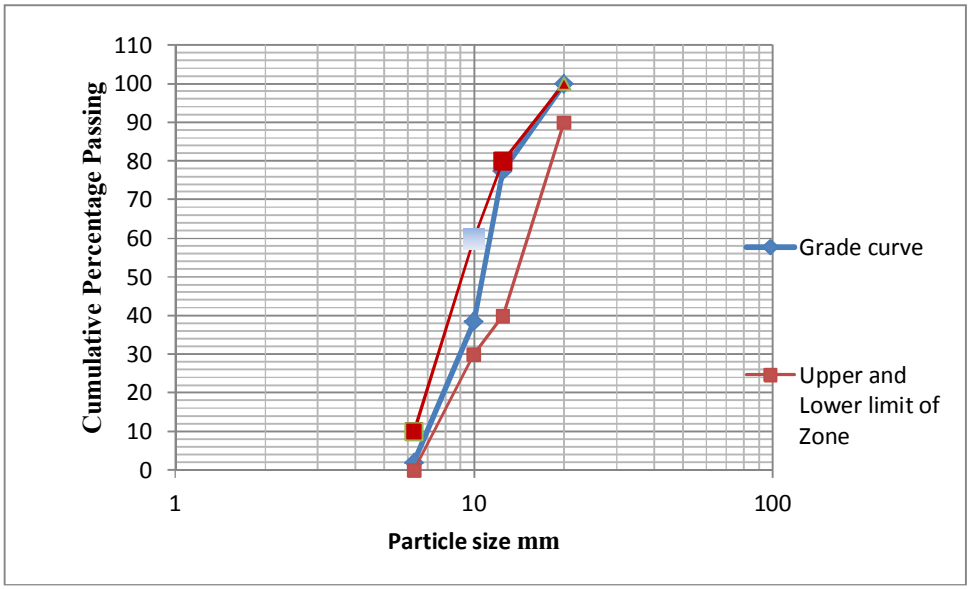


Fig. 4.1: Particle size distribution for coarse aggregates

4.3 Fine Aggregate:

Fine aggregate used consisted of river sand from river Rafin Yashi in Zaria. The result of the particle size distribution is presented in table 3.4 of chapter three. The sieve analysis was carried out in accordance with BS 812 (1975). A graphical presentation of the particle size distribution is shown in figure 4.1 below. The plot of the particle size distribution showed that it is within Grading Zone 1 of B.S. 882 (1973). It also shows that it is well graded.

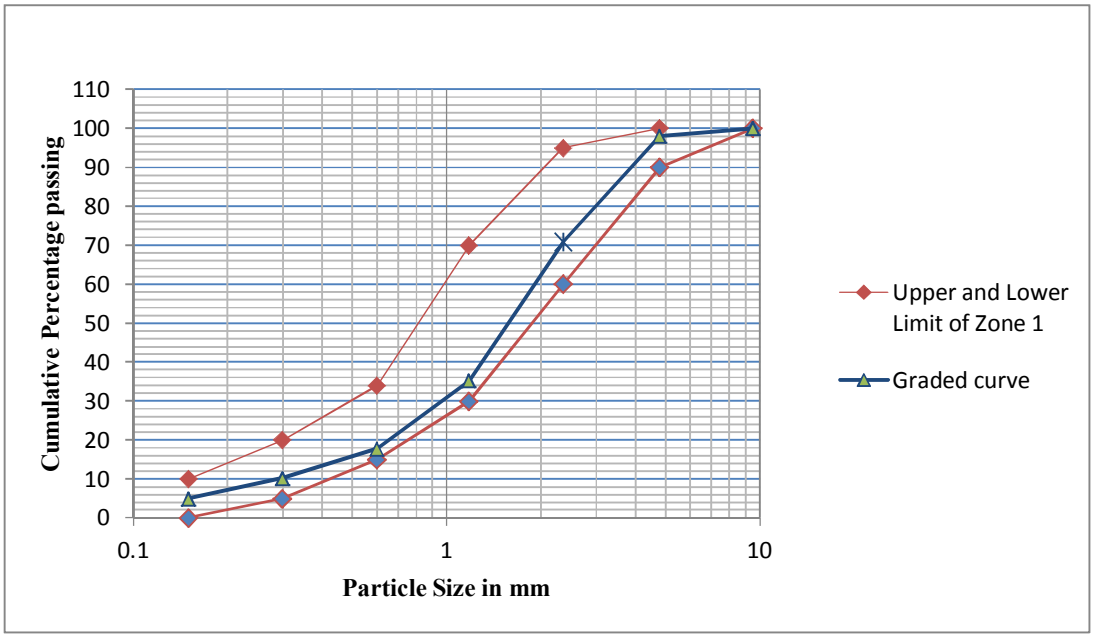


Fig. 4.2: Particle size distribution for fine aggregates

4.4 Cement (Consistency, Setting Time, and Soundness):

The use of cement requires stringent control, this is why it is necessary to determine the water content of the paste which will produce required consistence. The test was carried in accordance with BS EN 196 P3 (1995). The consistency obtained from the cement used (obtained from the average of three trial sample) was 30 per cent as shown in table 3.5 of chapter three. This is in agreement with the usual range of 26 and 33 per cent specified in BS 4550 (1978).

The experiments for setting time were carried out in accordance with BS EN 196 P3, 1995 and the results presented in table 3.6 of chapter three. The average of the initial setting times of all the samples presented in table 3.6 (46 min) was not below 45 minute and the final setting times (89 min) was below 10 hours. These results were in agreement with BS 12 (1978). The initial and final setting times of cement used agreed with the code specifications.

4.5 Corn Cob Ash:

The Corn Cob ash was analysed using an energy dispersive x-ray fluorescence (EDXRF) machine to determine the elemental and oxide composition of the ash in the Centre for Energy Research, Zaria. The oxide composition is presented in the table 3.8 of chapter three. The percentage composition of silicon dioxide (61.5%) is above the 25% range specified by BS EN 197-1:2000. Using the ASTM C618 for classifying pozzolanas, Corn cob ash is classified in class F pozzolana.

Table 4.1: Comparison of oxide composition of CCA and cement

	%SiO_2	**%Al_2O_3**	**%Fe_2O_3**	**%CaO**
Experimental (CCA)	**61.5**	**18.3**	**8.7**	**3.02**
Typical ordinary Portland	**18-22**	**2-5**	**2-6**	**62-66**

Table 4.1 above compares the oxide composition of corn cob ash and that of a typical portland cement. The total percentage of Iron Oxide, Silicon Oxide and Aluminium Oxide when added together was greater than the minimum 70% specified by for pozzolanas (ASTM 618, 2005). The high percentage of silicon oxide (61.5%) is beneficial in pozzolanic reaction with time.

4.6. Cement/ CCA Consistency Test:

The CCA / Cement samples were labelled D, E, F, G, and H. where sample D, was the control sample containing 100% cement content and E, F, G, and H represent samples with 10%, 20%, 30%, and 40% CCA/ Cement substitution. The test was carried in accordance with BS EN 197 P1 2000

Figure 4.3 shows the result from the standard consistency tests in table 3.9 of chapter three. From the results, it is clear that the consistency (amount of water required to achieve the standard consistency) ratio increases with the increasing of the CCA / cement substitution as shown in figure 4.3 below. This shows that CCA is a retarding agent.

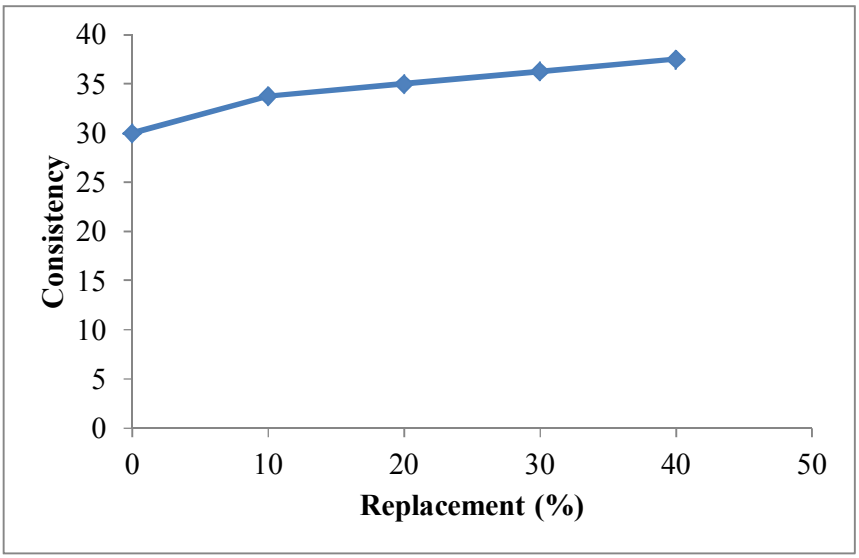


Fig. 4.3: Consistency of CCA cement

4.7 Cement/ CCA Soundness Test:

Soundness means the ability or otherwise of a cement to maintain a constant volume. Unsound cement will expand slowly and over a long period. The test was carried in accordance with BS EN 197 P1 2000. The results for soundness were presented in table 3.9 of chapter three. The results in table 3.9 are in agreement with the usual range of 26 and 33 per cent specified in BS 4550: part 3: section 3.5: 1978. Increase in CCA content up to 50% in CCA/ Cement mortar mixture satisfies requirements of BS 4550: part 3 for expansion. The result of the experiment is shown in table 3.9. The result shows a decrease in expansion with increase in CCA cement. This may also have been as a result of reduced cement content. All samples satisfied the code requirement that specifies that expansion shall not exceed 10 mm thus CCA/cement mix satisfied BS EN 197 P1 (2000) code for soundness.

4.8 Cement/ CCA Setting Time Test:

In the results for setting time presented in table 3.10 of chapter three, sample D represents the sample with 100% cement content while samples E, F, G, and H represents samples with 10%, 20%, 30% and 40% CCA/ Cement content. The initial setting time of all the samples presented in table 3.11 of chapter three (46, 48, 54, 93 and 116 min) were not below 45 minutes and the final setting time (85, 100, 130, 172 and 227 min) were not above 10 hours. These results were in agreement with BS 12: 1978 thus CCA/Cement mixture satisfied both requirement for initial and final setting presented by the code.

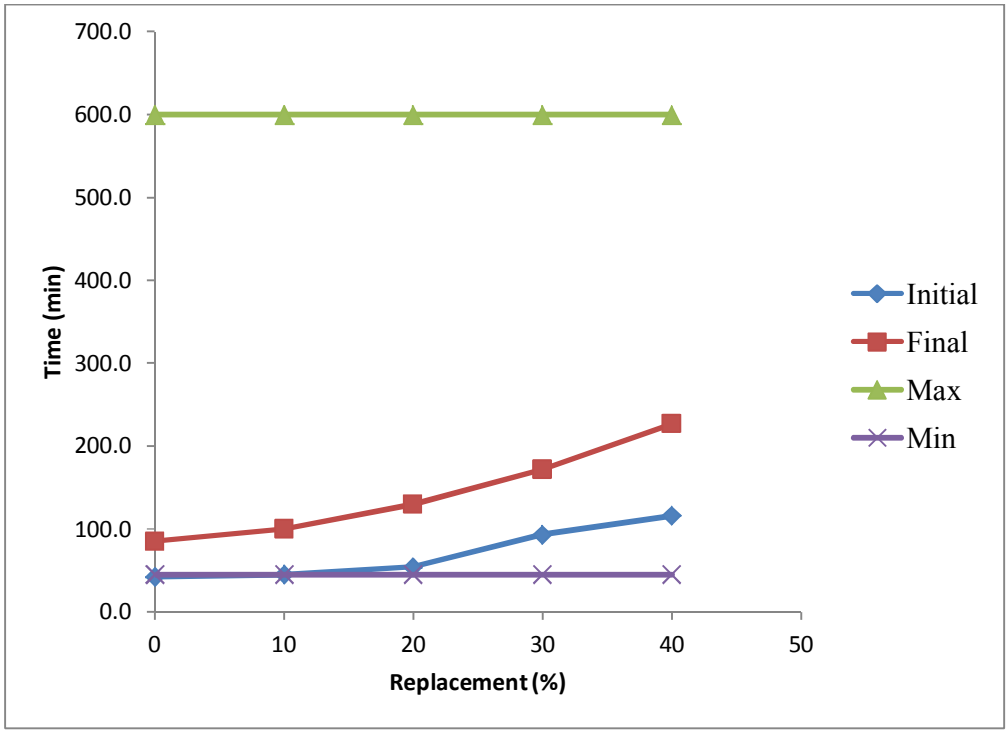


Fig.4.4. Initial and final setting times of CCA cement

The results of initial and final setting times of CCA/ Cement from table 3.10 are plotted in Figure 4.4 above. The result shows that setting times increased as the percentage of CCA in the mixture increased this shows that CCA has retarding properties. The increase in setting may have been due to reduced cement content in the mortar mixture. Also as shown in section 4.6, CCA increases the amount of water required to achieve standard consistency. Therefore, because of the increase in amount of water, it is expected that the amount of time required for the cement to set should increase. From the figure 4.4 above, it can be seen that as the percentage CCA content increased, the difference between initial setting and final setting also increased. This can

be attributed mainly to the reduced cement content in each mix as the percentage CCA increased.

4.9 Concrete Made from Cement / CCA Mixture

4.9.1 Density of Cubes

In this study, CCA was used to substitute cement in the preparation of concrete cubes. The specimens were prepared as described in section 3.9 of chapter three. The specimens were weighed at 1, 3, 7 and 28 days. The density of the specimen at these ages was then computed as shown in table 3.16 of chapter three. The results are presented in figure 4.5 and 4.6 below. The Corn Cob Ash substitution, in the considered range had some effect on density of cubes.

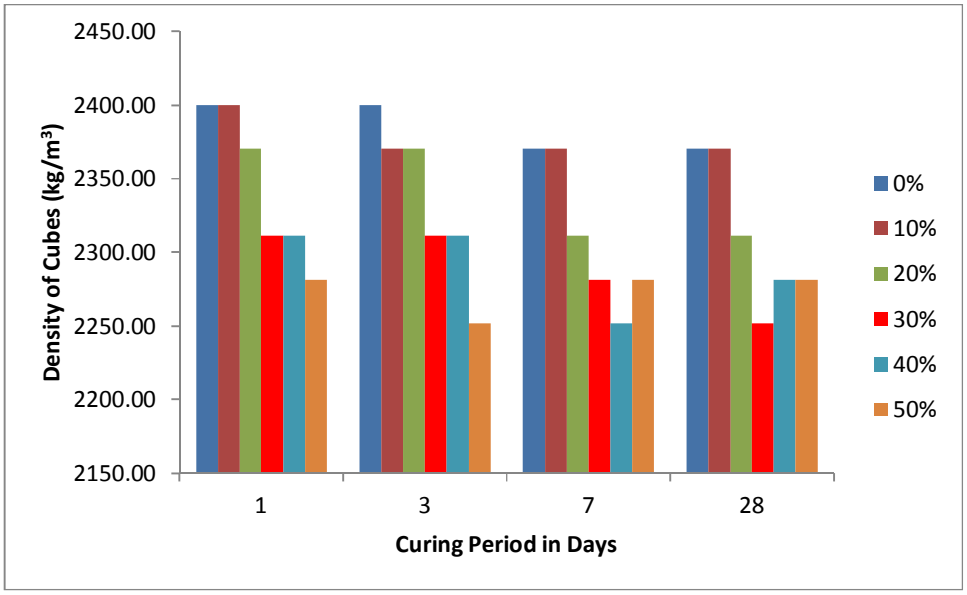


Figure 4.5: Density of cubes versus curing age for CCA/ Cement

From Figure 4.5 above, it can be seen that for the control (0% ash content) and for CCA/ Cement concrete specimens, the bulk density decreased with age of curing. It

however drops sharply at age of 7 days and continues to decrease steadily. This is because as the concrete hardens it uses up water in hydration, and the products of hydration occupy less space than the original water and cement (Neville, 1995).

From figure 4.6, the results show that for the same age, the bulk density decreases as the proportion of CCA increases in concrete specimens. This may be because ordinary Portland cement has a higher specific gravity (3.15) than corn cob ash (2.15). For this case the density is decreasing steadily as CCA is increasing. At age 3 days, the density of cube specimen containing 10% and 20% CCA were the same. The same condition also occurs between cube specimen containing 30% and 40% CCA at age 3 days. At age 28 days, the density of specimen containing 0% and 10% CCA were the same. The same situation occurs for cube specimen containing 40% and 50% CCA content at age 28days.

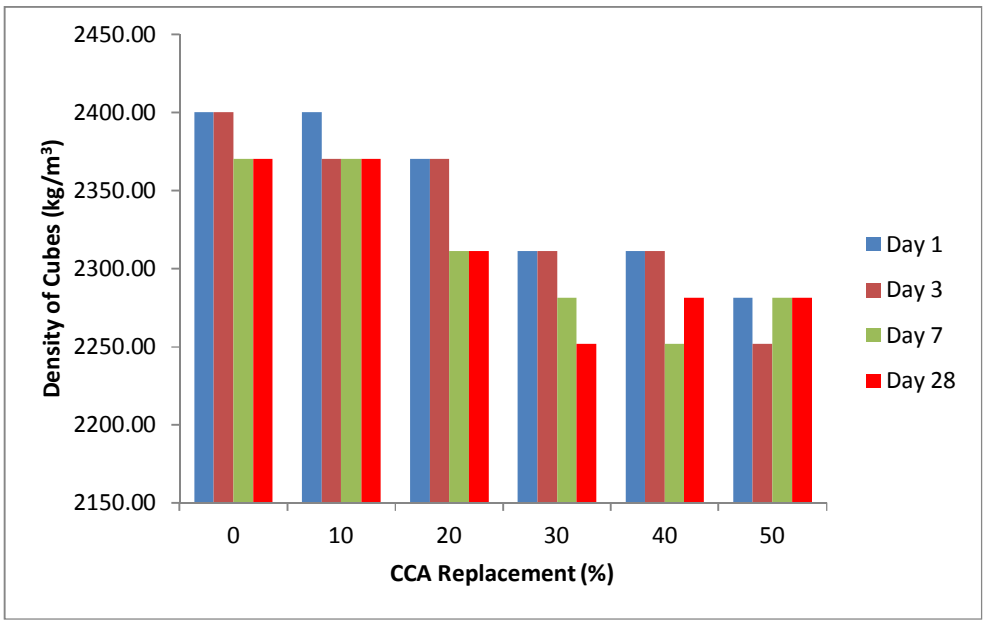


Figure 4.6: Density of Cubes with increasing Ash/ cement replacement

4.10 Compressive Strength Test CCA/Cement Concrete Cubes

In this study, CCA was used to substitute cement in the preparation of concrete cubes. The specimens were prepared as described in section 3.9 of chapter three. Figure 4.7 shows the results for the compressive strength of Corn Cob Ash / OPC concrete at 1, 3, 7, and 28 days. The result shows that the cubes containing 0% Corn Cob Ash had the highest compressive strength. This is due to the fact that the cement content per m^3 for this mix was the highest. The results also show that for the same age, the compressive strength decreases as the proportion of CCA/ Cement content increases as seen in figure 4.7 below.

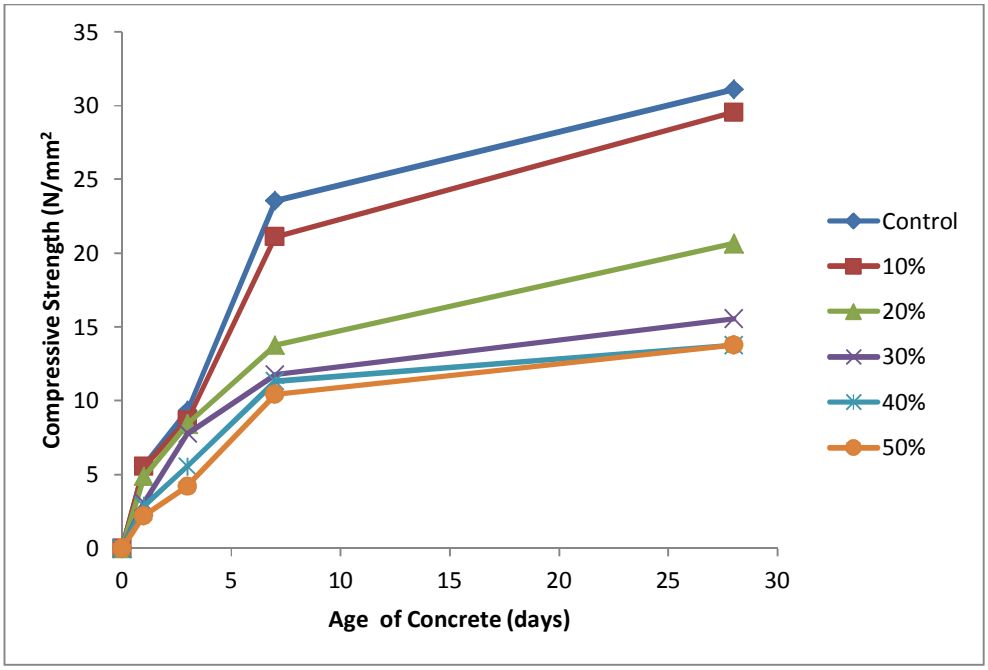


Figure 4.7: Compressive strength of Cement /Ash Concrete

From figure 4.7 above, it can be seen that the curves are parabolic like any concrete material. The rate of increase in compressive strength with age is rapid within the first seven days, it then increases gradually at a diminishing rate until 28 days.

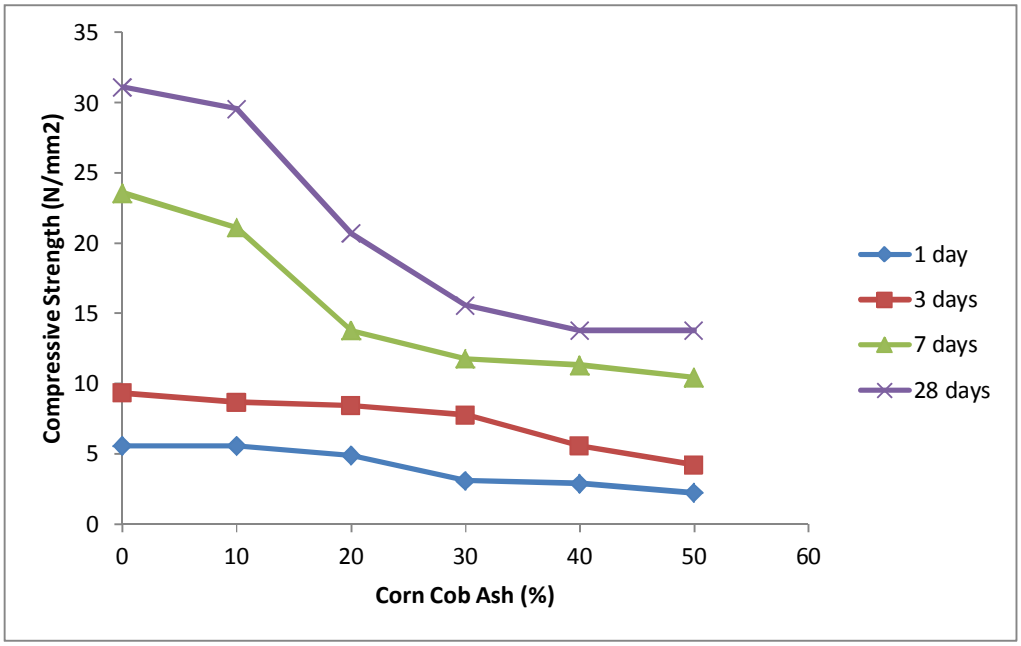


Figure 4.8: Compressive Strength of Concrete with Various Percentage of CCA

From figure 4.8 above, as the percentage of CCA content in the concrete increases, the compressive strength decreases. For the control cube, (0% ash and 100% cement) strength increased from 23.56 N/mm^2 at 7 days to 31.11 N/mm^2 at 28 days. For CCA modified concrete sample containing 10% ash and 90% cement, the compressive strength increased from 21.11 N/mm^2 at 7days by about 29.56 N/mm^2.

According to BS 8110 part 2 (1985), a grade 30 concrete mix design without any blending of the cement should have acquired a strength of 20 N/mm^2 within the first seven days of wet curing and 30 N/mm^2 within 28 days. Based on the above and the result obtained from this work, 10% ash and 90% cement can be suitable for use in concrete.

FAO, (1986) reported that cement blended with pozzolanas would produce 65 to 95 % strength of OPC concrete in 28 days. Further, they reported that their strength normally improves with age since pozzolanas react more slowly than cement due to different composition and at one year about the same strength is obtained. This behaviour was confirmed by Sideris and Sarva, (2001) and Sengul, et al. (2005). Results obtained from this study have shown similar patterns. Specimens containing up to 20% CCA had compressive strength of 20.67 N/mm^2 and this exceeded 65% of the 28 day compressive strength (31.11N/mm^2). Similarly, CCA concrete samples containing 10% ash and 90% cement produced compressive strength higher 65% of OPC concrete in 28 days.

4.11 Effect of Acid on CCA/ Cement Concrete

Acid resistance is one of the required properties for structural materials used in aggressive environments. It is known that Portland cement concrete does not possess a high acid resistance due to its chemical composition that includes high-calcium compounds. Cube specimens containing CCA/ Cement in different proportions as described in section 3.9 were cured in 5% and 10% concentrations of Sulphuric acid, Acetic acid and sodium Sulphate solution for 60 and 90 days. The effects of the acid on the samples and the effect on the compressive strength were investigated and discussed in the sections below.

(a) **Loss of Weight**

The details on the loss of weight of concrete cube specimens at different periods of exposure up to 1440 hour (60 days) in different acid solutions are shown in the tables 3.21 to 3.26 of chapter three. From tables 3.21 to 3.26 of chapter three, it is clear that control cube and those prepared with CCA as a partial replacement for cement all showed mass change (Loss of weight with age). These trends are better seen in the figures 4.9 to 4.13 below. In figures 4.8 to 4.12 below, the average weight loss of samples in the same medium is plotted against percentage CCA content and trend lines are used to show actual direction of the plot. The trend line is an upward or downward line on the chart indicating movements of average weight loss over a period of time. This is easily achieved using the excel work sheet.

i. **Loss of Weight in Sodium Sulphate Solution:**

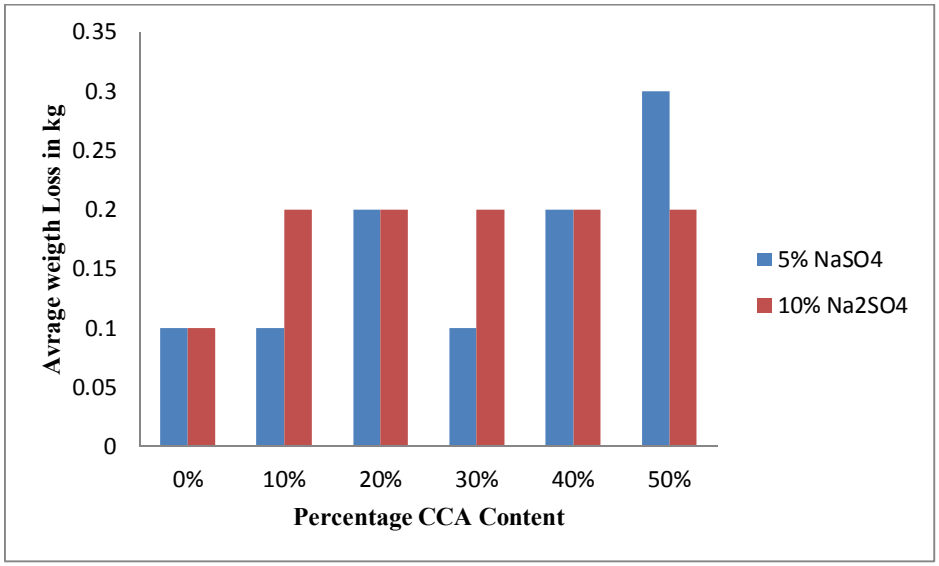


Figure 4.9: Average weight loss of cubes cured in 5% and 10% Sodium Sulphate Solutions

The loss of weight in this experiment could be attributed to the eating away of the hydrated cement paste and leaving cohesion less granular mass (Zivica, Bajza, 2001). The trend lines plotted from the scatter diagram in figure 4.9 above show that the loss of mass increases with increasing CCA content. From the trend lines, the control samples (0% CCA) had the lowest weight loss while samples with 50% CCA had the highest weight loss. This may also have been due to the reduced amount of binder (cement) in the mix. Control samples containing 0% CCA showed better resistance (Lower weight loss) in Sodium sulphate solution as compared to samples containing CCA.

ii. **Loss of Weight in Sulphuric Acid Solution**

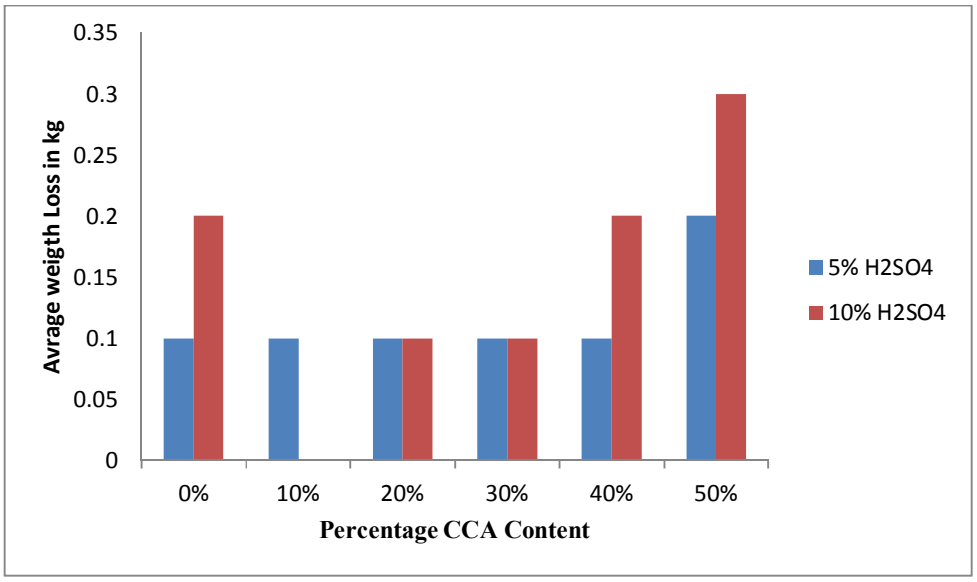


Figure 4.10: Average weight loss of cubes cured in 5% and 10% Sulphuric acid Solutions

The loss in weight of the samples that were exposed to sulphuric acid was relatively lower than in other acidic solutions (See figure 4.10 above). This may have been due to calcium sulphate (gypsum) formed due to the reaction between sulphuric acid and cement and this is less soluble in water. Solubility of calcium sulphate, was 0·20 % (by weight). Zivica (2001). Due to this fact, the weight loss of samples that were cured in sulphuric acid solution was low. However the linear trend lines shown in figure 4.10 indicate that weight loss in sulphuric acid solution approximately increased as CCA content increased. From the trend lines, samples with 20% CCA had the lowest weight loss while samples with 50% CCA had the highest weight loss.

iii. **Loss of Weight in Acetic Acid Solution**

Concrete is attacked by acetic acid which combine with free lime ($Ca(OH)_2$) in the concrete, producing highly soluble calcium salts. These salts enter the pore structure of the concrete, lowering the pH of the pore solution and allowing corrosion of the paste. This process lead to the loss of weight in specimens cured in acetic acid solutions (De Belie, et al, 1997). Figure 4.11 below shows trend lines for specimens cured in acetic acid. From the trend lines it can be seen that weight loss increases as CCA content increases. From the trend lines, the control samples (0% CCA) had the lowest weight loss while samples with 50% CCA had the highest weight loss. This may also have been due to the reduced amount of binder (cement) in the mix.

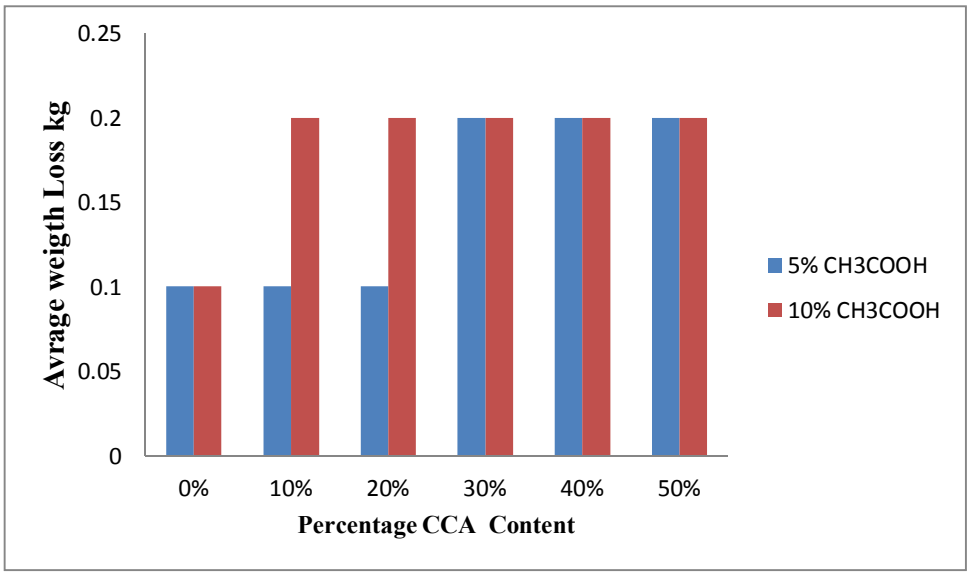


Figure 4.11: Average weight loss of cubes cured in 5% and 10% Sulphuric acid Solutions

A comparison of average weight lost by concrete cubes cured in 5% and 10% solution of different aggressive media is shown in figures 4.12 and 4.13 below. Linear trend lines are used to better describe the behaviour of the scatter diagrams. From the trend lines, it is clear that the loss in weight of the samples that were exposed to sulphuric acid was lowest while samples cured in sodium sulphate showed greater deterioration. In 5% solution of Sodium sulphate, sulphuric acid, and acetic acid, sodium sulphate solution had a greater effect on weight loss on CCA modified concrete.

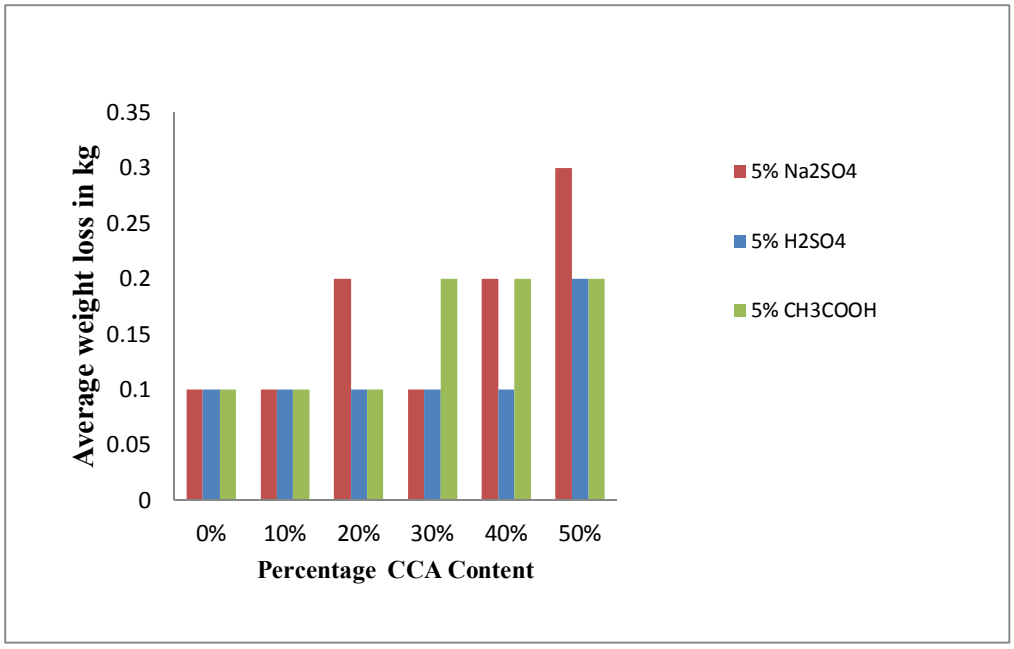


Figure 4.12: Average weight loss of cubes cured in 5% acid solutions

Linear trend lines have also been used to better describe the behaviour of the scatter diagrams of specimens cured in 10% solutions of different acids. From the trend lines, it is clear that the loss in weight of the samples that were exposed to sulphuric acid was lowest while samples cured in sodium sulphate and acetic acid showed greater deterioration. In 10% solution of Sodium sulphate, sulphuric acid, and acetic acid, sodium sulphate and acetic acid solutions had a greater effect on weight loss on CCA modified concrete.

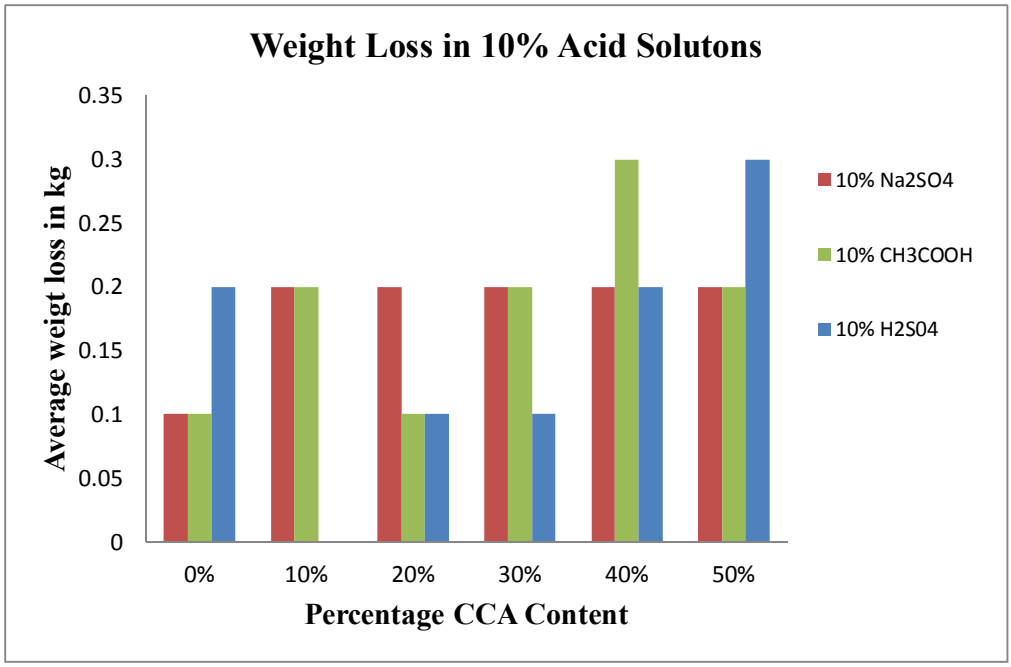


Figure 4.13: Average weight loss of cubes cured in 10% acid Solutions

4.12 Visual Inspection

Plates A_{3-1} to A_{3-36} in appendix A3, shows pictures taken of cube specimens cured in 5% and 10% solutions of Acetic acid, Sulphuric acid and sodium sulphate. For each sample, a typical cube specimen was selected and photographed. The title below the cube specimen also indicates the percentage CCA content. Some of the selected photographs are presented in plates 4.1 to 4.6 below.

For each set of specimen i.e. cured in 5% H_2SO_4 solution and 10% CH_3COOH acid solution etc. It can be seen clearly that as the percentage CCA content in concrete specimen increases, the surface deterioration of the sample increases for the same acid concentration. Samples cured in sodium sulphate solution (plates A_{3-13} to A_{3-24} of appendix A3) had a whitish surface. This may have been because of gypsum or salt that formed at the surface of the specimen.

As can be observed on plates 4 A_{3-13} to A_{3-36} of appendix A3, there is a deepening in the greyish colour of samples as the CCA content increases. This is principally because the colour of CCA is grey and as its percentage in the mix increases, its colour dominance increases.

Generally the surface deterioration observed on the surfaces of the control samples and samples with 10% CCA content were much less than samples with higher CCA content. Surface deterioration of samples with more than 30% CCA content increased as percentage CCA content increased when exposed to the acid solution.

Samples cured in acetic acid solutions generally had a reddish surface colour plates A_{3-25} to A_{3-36}. All samples exhibited changes in colours and Conner losses due to the effect of the acid. In addition, parts of the cement paste were also lost as the surface of the concrete softened.

All test samples showed a minor degree of dissolution at their corners. This is principally because acids used to cure samples i.e. sulphuric acid, and acetic acid are

very aggressive as their calcium salts are readily soluble and removed from the attack front (De Belie, et al, 1997). (Zivica, Bajza, 2001).



Plate 4.1: 50% CCA Replacement in 5% H_2SO_4



Plate 4.2: 50% CCA Replacement. in 10% H_2SO_4



Plate 4.3: 50% CCA Replacement in 5% Na_2SO_4



Plate 4.4: 50% CCA Replacement in 10% Na_2SO_4



Plate 4.5: 50% CCA Replacement in 5% CH_3COOH



Plate 4.6: 50% CCA Replacement in 10% CH_3COOH

4.13 Compressive Strength

At the end of the curing period (specimens soaked in acid solution), specimens were tested in compression to determine their residual strength. Specimens that were cured in water were also tested at the same time for comparison purpose. The relationship between the compressive strength for the cubes cured in acid solution and the specimens cured in water are compared. Comparisons between specimens containing 10%, 20%, 30%, 40% and 50% CCA cured in the same solutions (i.e. water or acid) are also compared.

(a) Compressive Strength of Specimen Cured in 5% and 10% Solution of Sodium Sulphate.

Because of the slow rate of deterioration in acidic solutions and continued hydration of the cement, strength of cubes were consistently higher after 90 day curing period both in 5% and 10% Sodium Sulphate solutions (See figures 4.14 and 4.15 below). The continued reaction of silicon oxide with calcium hydro-oxide from the hydration of cement in concrete could also have added to the increased 90 days strength. A closer look at figures 4.14 and 4.15 below, it was observed that for specimen containing less than 30% CCA, compressive strength at 60 days curing period was equal to or higher than compressive strength at 90 days curing period for the same CCA content. This behaviour can be attributed jointly to the reduced cement content per m^3 and aggression of the solution on the samples.

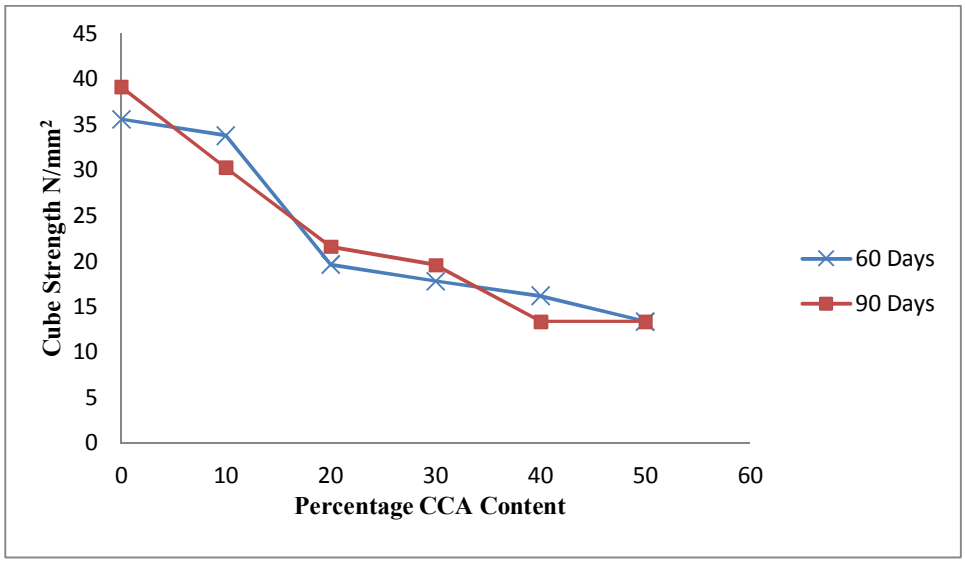


Figure 4.14: Compressive strength of specimens cured in 5% sodium sulphate solution

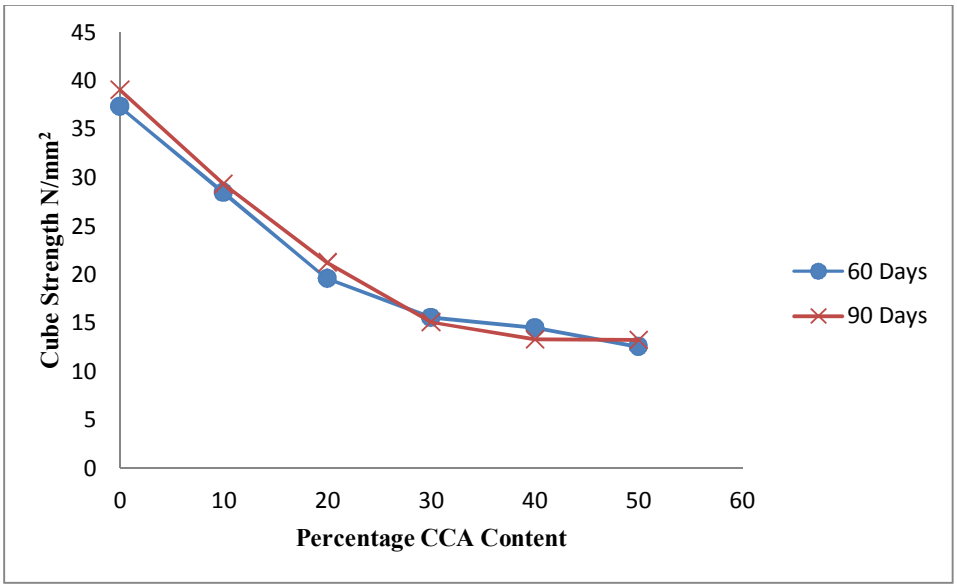


Figure 4.15: Compressive strength of specimen cured in 10% sodium sulphate solution

(b) Compressive Strength of Specimen Cured in 5% and 10% Solution of Sulphuric Acid

For the cubes cured in sulphuric acid solution, the 90days compressive strength was higher than the 60 days compressive strength. The continued reaction of silicon oxide with calcium hydro oxide from the hydration of cement in concrete may have added to the increased 90 days strength. This can be seen from figures 4.16 and 4.17 below. Also the formation of gypsum with low solubility around the cubes may have reduced the rate of deterioration of the samples thereby increasing the strength. Generally cube strength decreases with increase in CCA content.

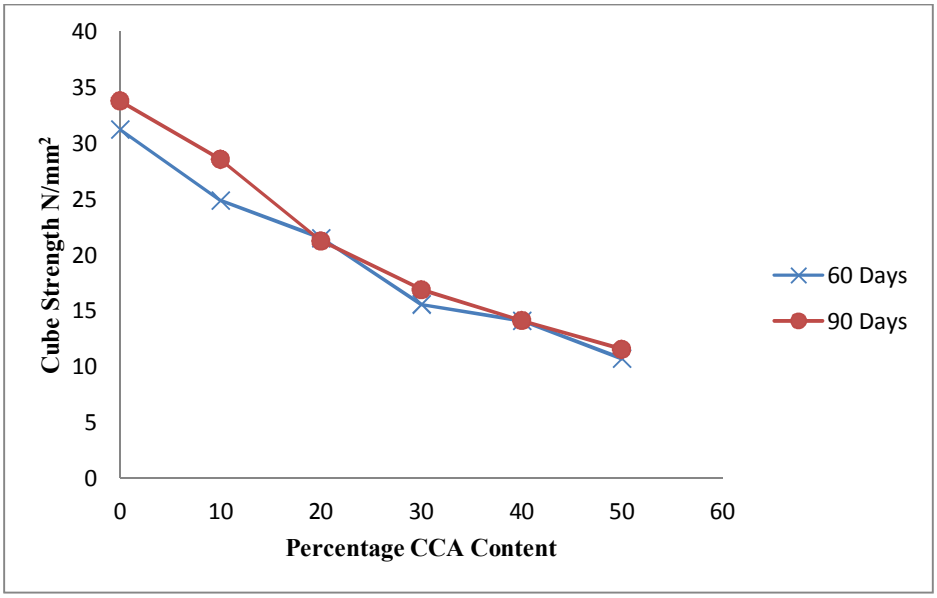


Figure 4.16: Compressive strength of concrete cured in 5% Sulphuric Acid solution

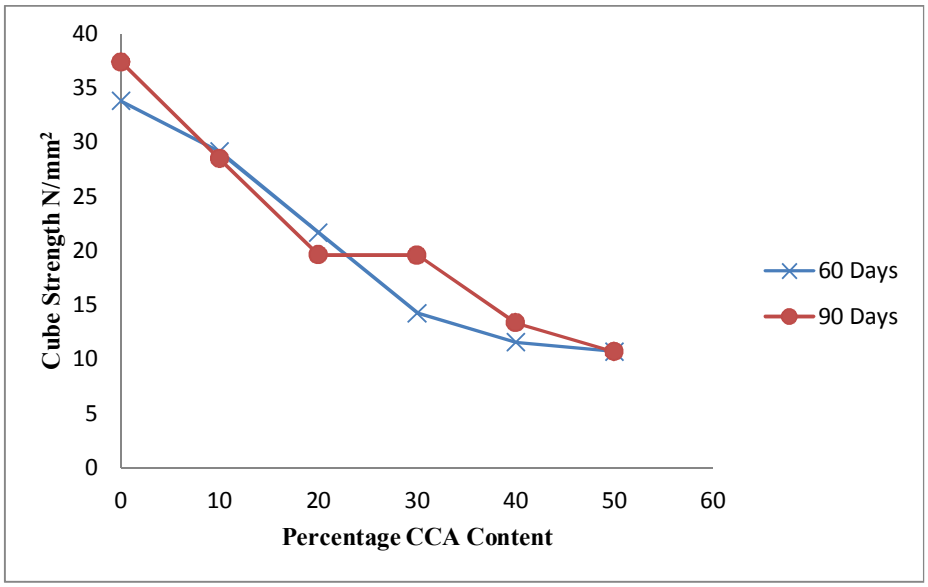


Figure 4.17: Compressive strength of concrete cured in 10% Sulphuric Acid solution

(c) Compressive Strength of Specimen Cured in 5% and 10% Solution of Acetic Acid

From the figure above it can be seen that the compressive strength of specimen decreases with an increase in CCA content. Concrete attacked by acetic acid combines with free lime ($Ca(OH)_2$) in the concrete, producing highly soluble calcium salts. These salts enter the pore structure of the concrete, lowering the pH of the pore solution and allowing corrosion of the paste. This process leads to the loss of weight in specimens cured in acetic acid solutions (De Belie, et al, 1997). A close look at figures 4.18 and 4.19 below it can be seen that there was no clear difference in compressive strength of specimens at 90 days and those of 60 days up to a CCA content of 30% after which there is a close comparison for CCA content for 40% and 50%. The explanation for this behaviour is that there is a lower binder content and increased deterioration of samples due to the presence of acidic environment.

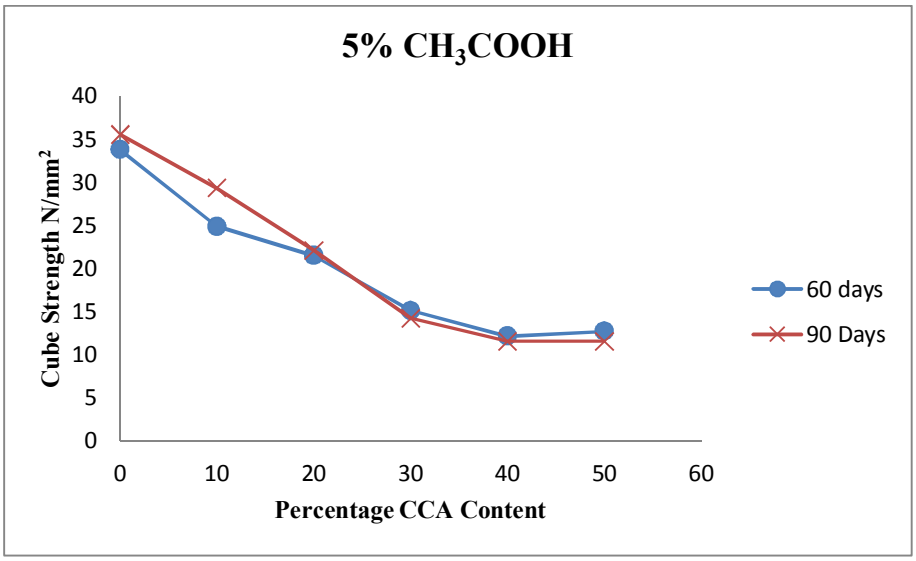


Figure 4.18: Compressive strength of concrete cured in 5% Acetic Acid solution

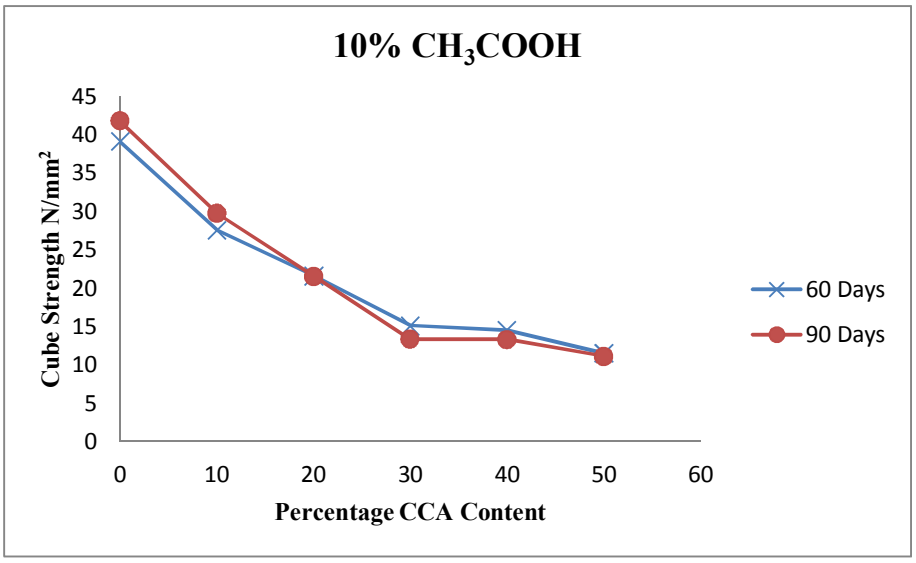


Figure 4.19: Compressive strength of concrete cured in 10% Acetic Acid solution

(d) Comparison of Compressive Strength of Samples Cured in Aggressive Solutions and Samples Cured in Water at 60 and 90 Days

Comparison is now made between Companion specimens that have been continuously cured in water which served as the controls, with specimens cured in different acid solutions but for the same curing period. The relationship between the strength for the cubes exposed in acid solution and the specimens stored in water are shown in figures 4.20 and 4.23 below.

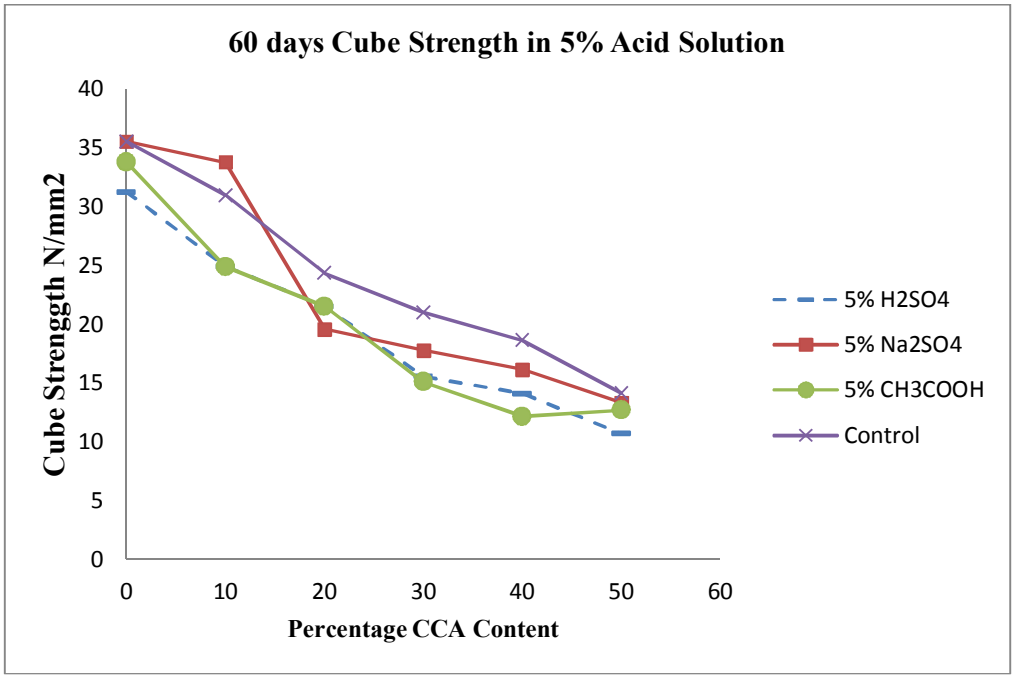


Figure 4.20: Comparison of Compressive strength of concrete cured for 60 days in 5% acid concentration of different acidic media.

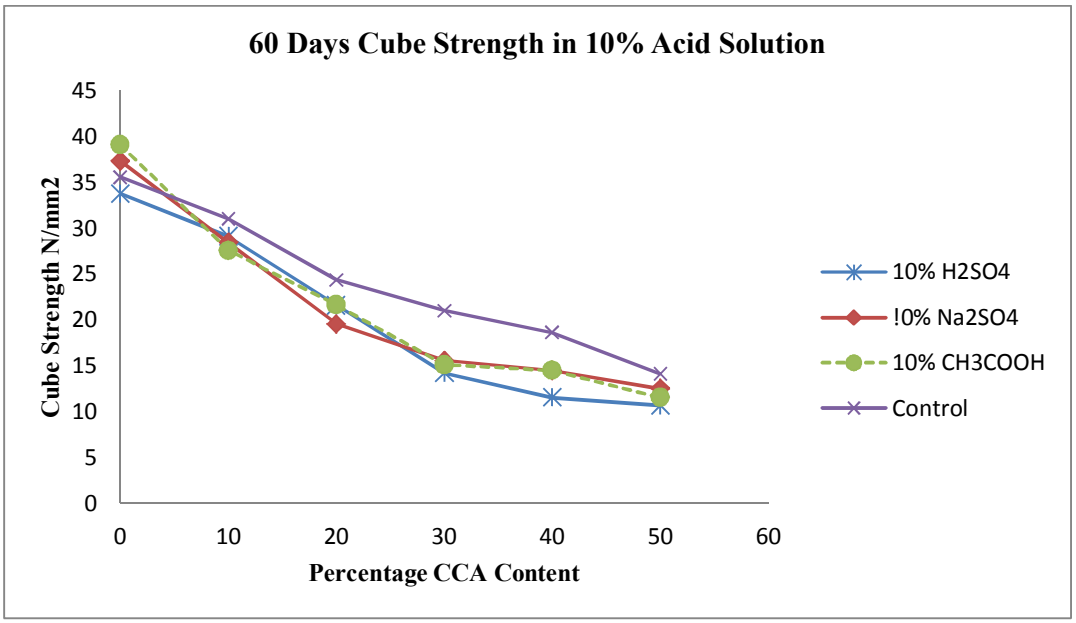


Figure 4.21: Comparison of Compressive strength of concrete cured for 60 days in 10% concentration of different acidic media

For samples with the same percentage CCA content, cubes cured in water had a higher compressive strength than cubes cured in acid solutions at 60 days (See figures 4.20 and 4.21 above). Cubes cured in sodium sulphate, acetic acid and those cured in sulphuric acid solution had compressive strengths that were very close. Specimen cured in sulphuric acid solution generally had the lowest strengths for the same age and CCA content. This can be seen in figures 4.20 to figure 4.21.

For samples with the same percentage CCA content, cubes cured in water had a higher compressive strength than cubes cured in acid solutions at 90 days (See figures 4.22 and 4.24 below) This may have been due to acidic attack on the cubes by the various aggressive environments they were subjected to. Cubes cured in acid solutions had comparative compressive strengths.

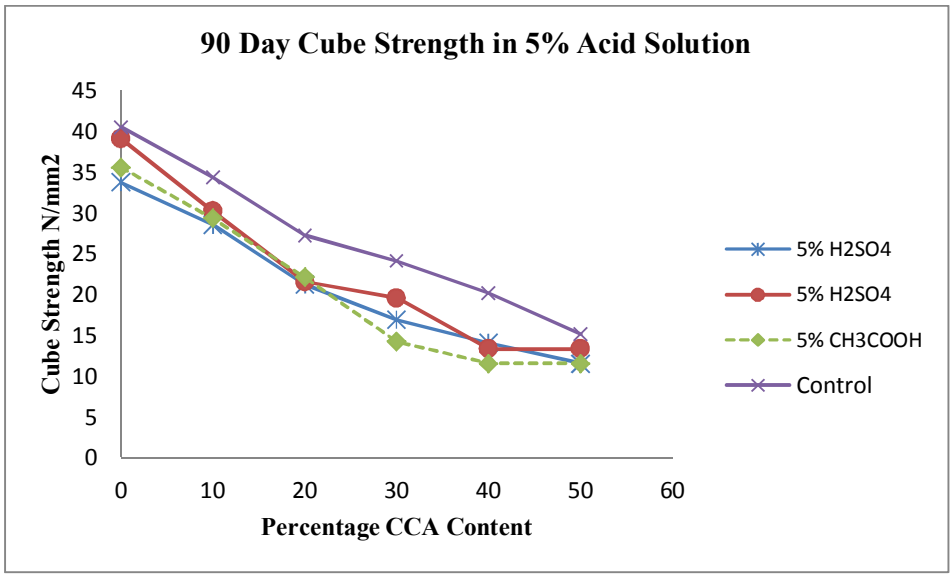


Figure 4.22: Comparison of Compressive strength of concrete cured for 90 days in 5% Concentration of different Acidic Media

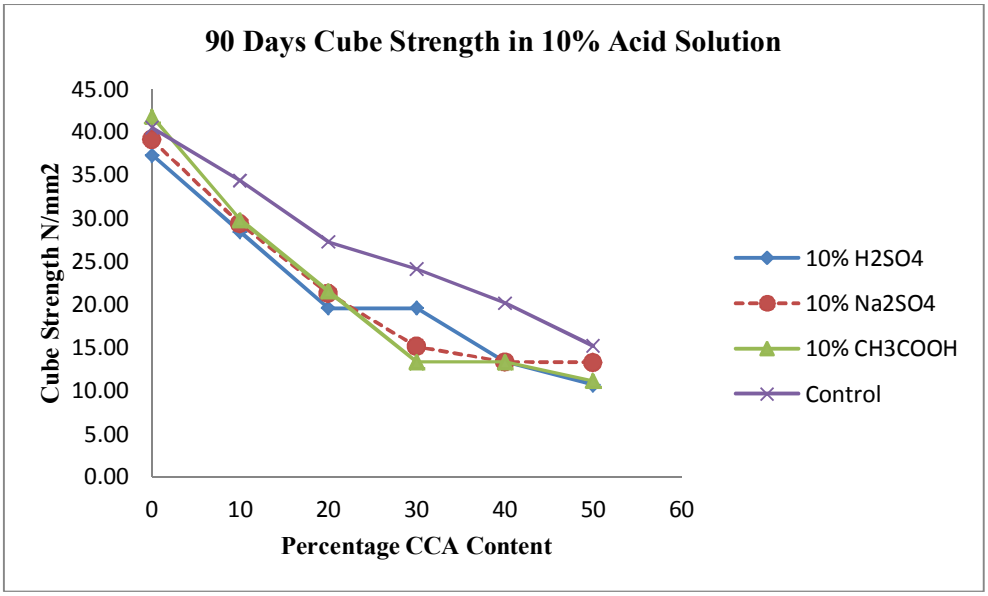


Figure 4.23: Comparison of Compressive strength of concrete of the same age Cured in 10% Concentration of Different Acidic Media

4.13.1 Loss in Compressive Strength

The loss of compressive strength (Compressive strength of control sample less the compressive strength of sample cured in acid solution at the same age) of concrete cubes with different CCA content immersed in 5% and 10% solutions of Sodium Sulphate, Sulphuric acid, and Acetic acid solutions at 60 and 90 days respectively were compared in Figures 4.24 to 4.26 below.

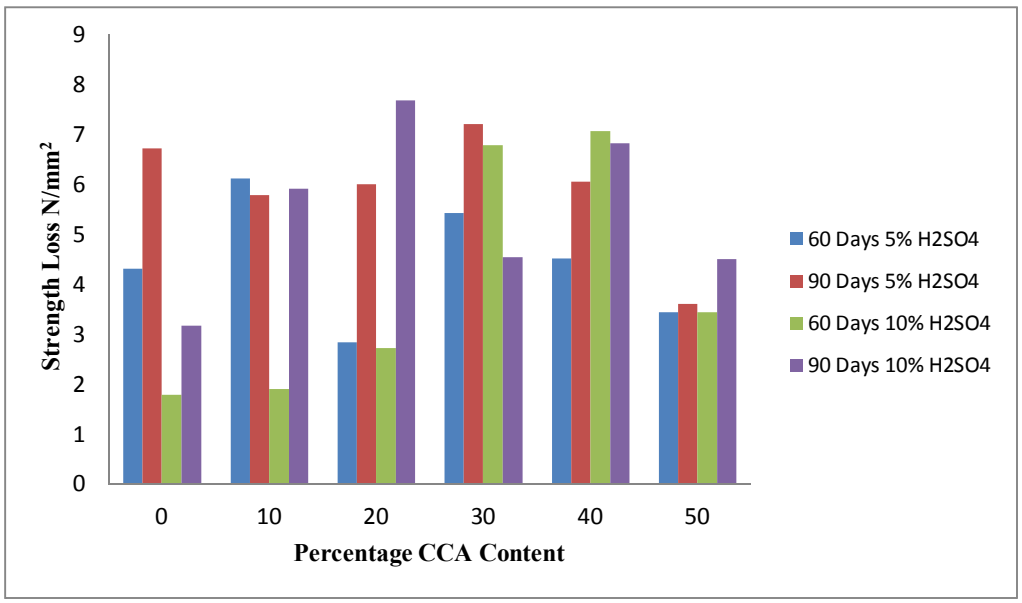


Figure 4.24: Comparison of Compressive strength Loss of concrete Cubes cured in H_2SO_4 Solution.

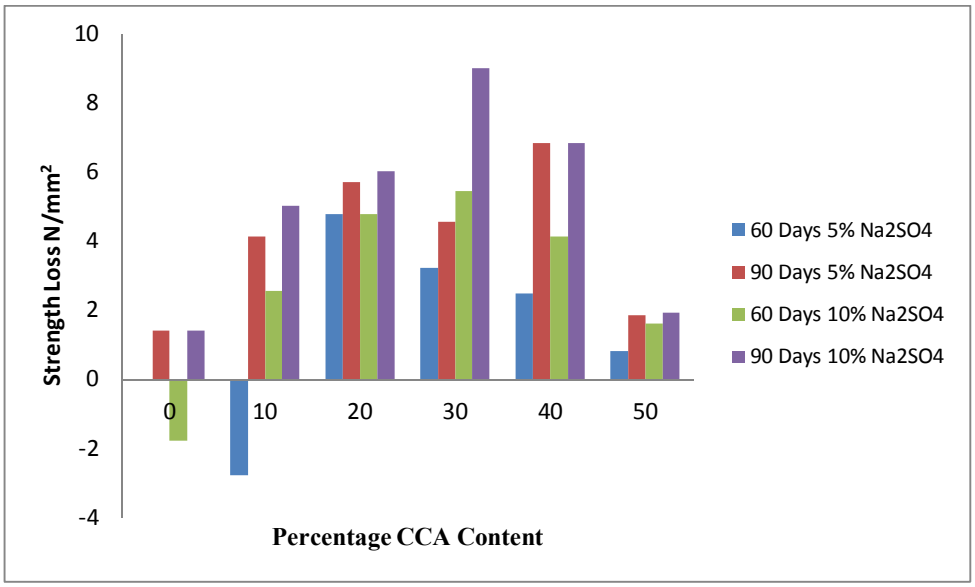


Figure 4.25: Comparison of Compressive strength Loss of concrete Cubes cured in Na_2SO_4 Solution.

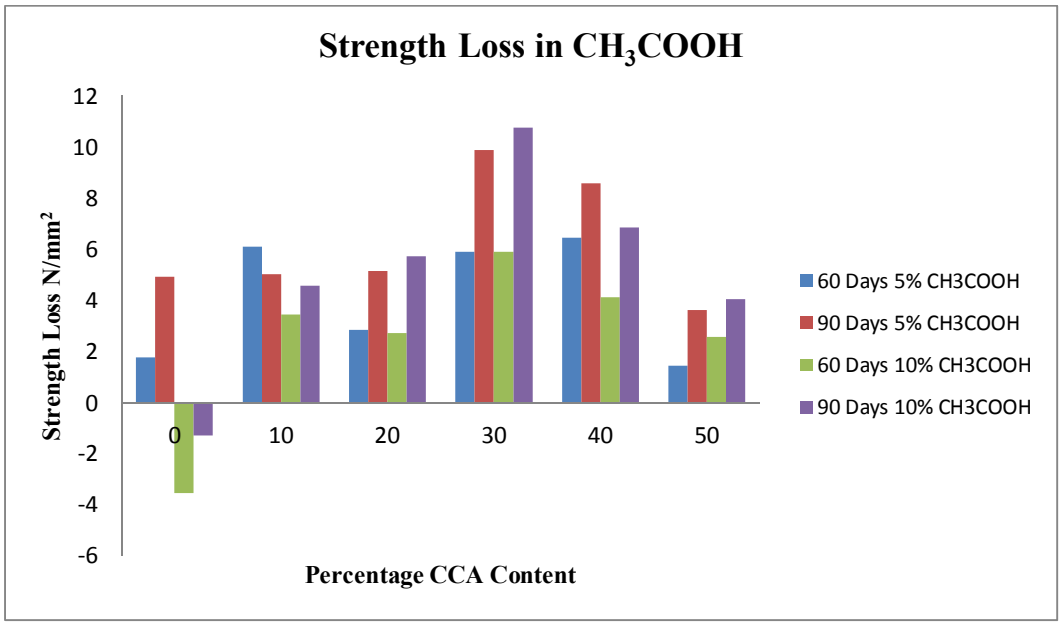


Figure 4.26: Comparison of Compressive strength Loss of concrete Cubes cured in CH_3COOH Solution.

The loss in compressive strength of concrete cubes at 60 days was lower than that for 90 days curing period in the same acid solution with the same concentration (figures 4.24 to 4.26). The higher loss in compressive strength with curing period at 90 days was due to the effect of the acid solution on the cubes. Prolonged stay caused increased deterioration.

The loss in compressive strength of cubes in solution with 10% concentration was higher than that of 5% concentration of the same solution (figures 4.24 to 4.26). This is in agreement with general principles that increased concentration of acid solution leads to faster deterioration.

Figures 4.27 and 4.28 below shows a comparison of strength loss of concrete cubes of the same age but cured in different acidic media with different concentration.

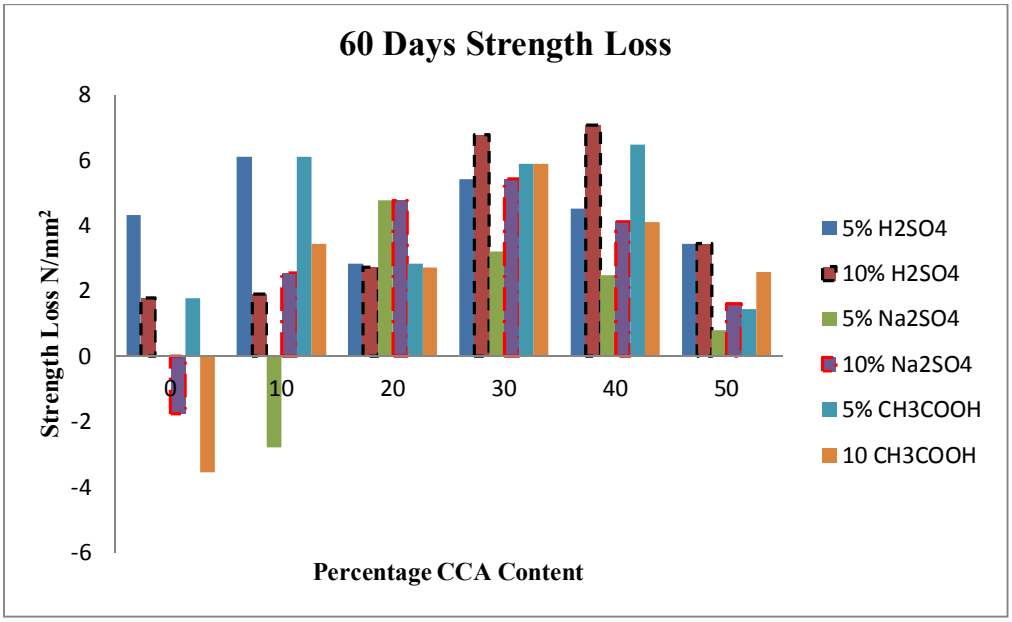


Figure 4.27: Comparison of Loss of Compressive strength of concrete of the same age Cured in 5% & 10% Concentration of Different Acidic Medium at 60 days

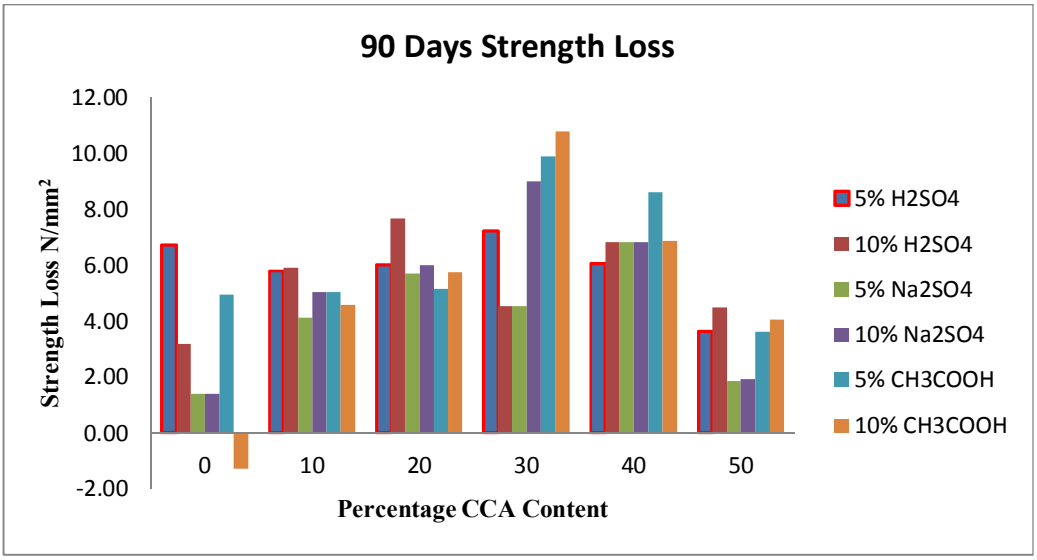


Figure 4.28: Comparison of Loss of Compressive strength of concrete of the same age Cured in 5% and 10% concentration of Different Acidic Medium at 90 days.

For the same strength of acid concentration, samples cured in Sulphuric acid had the highest reduction in strength followed by those cured in Acetic acid and the least were for the cubes soaked in Sodium sulphate solution regardless of the age (Figures 4.27 and 4.28). From this result it can be said that Sulphuric acid was the most aggressive to concrete. In some isolated case for control cubes cured in acid solution, the strength of the samples cured in acid solutions exceeded those of the control cured in water. This isolated cases shows that other factors affect the strength behaviour of concrete in aggressive environments i.e. compaction, amount of cement per m^3 etc. in another isolated case for cubes soaked in 5% sodium sulphate solution, for 10% CCA content, the strength exceeded the control. At this point it is necessary to mention that reaction between silicon oxide and calcium hydroxide contributed to the increase in strength of the test sample.

4.14 Regression Models for Compressive Strength of Concrete with CCA Content

For predicting compressive strength of concrete with CCA content, mathematical model describing the changes in strength (function Y) in dependence on selected factors was developed. Only the effect of the quantitative factors was taken into account: Percentage CCA content, (factor X1) and the time of curing (factor X2), separately for each type of curing media.

For mathematical model elaboration of the following factor levels, significant for practice, were selected:

- Factor X1: 0, 10, 20, 30, 40, 50
- Factor X2: 60, 90 days.

As the function describing the compressive strength development, a polynomial was assumed. The values of regression equation's coefficients were determined using the least-squares method. The calculations were conducted using the Microsoft Excel office package (Office 2010). First the actual experimental values were plotted. Next trend lines that best fit the plotted experimental curves were generated using excel package. Plots showing the actual observed values, the trend lines and the equations of the trend line in different chemical solutions are computed and presented in figures 4.29 to 4.35

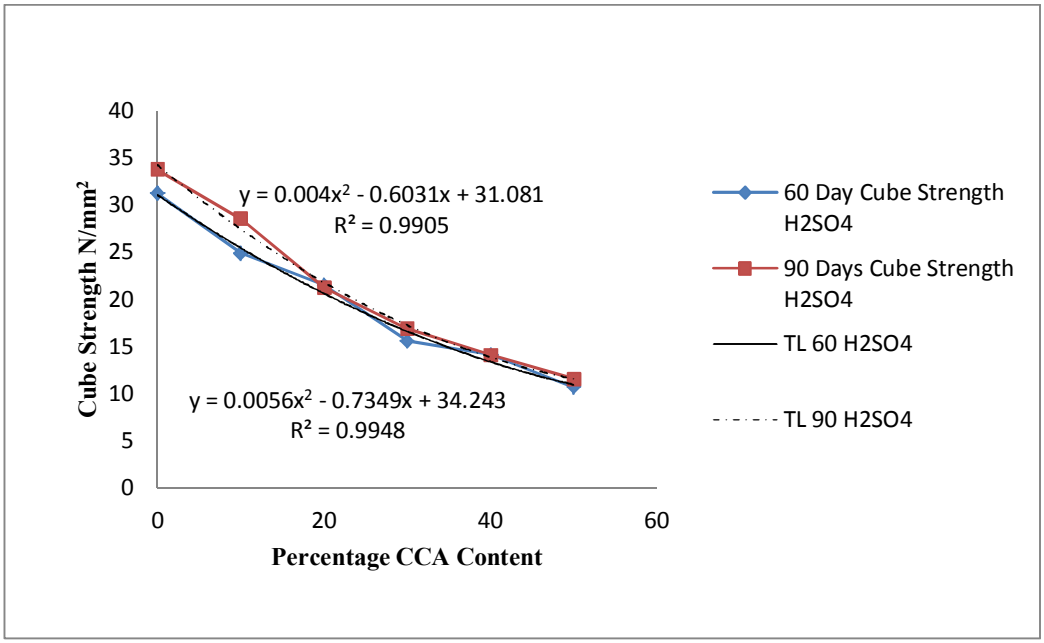


Figure 4.29: Graph for compressive strength of concrete with varying percentages of CCA content at 60 and 90 day curing period in 5% Sulphuric acid solution.

5% H_2SO_4 Solution	60 Days	$y = 0.004x^2 - 0.603x + 31.08$ $R^2 = 0.990$	Computed compressive strength in (N/mm^2) 31.08	Experimental value of compressive in (N/mm^2) 31.25
5% H_2SO_4 Solution	90 Days	$y = 0.005x^2 - 0.734x + 34.24$ $R^2 = 0.994$	34.24	33.78

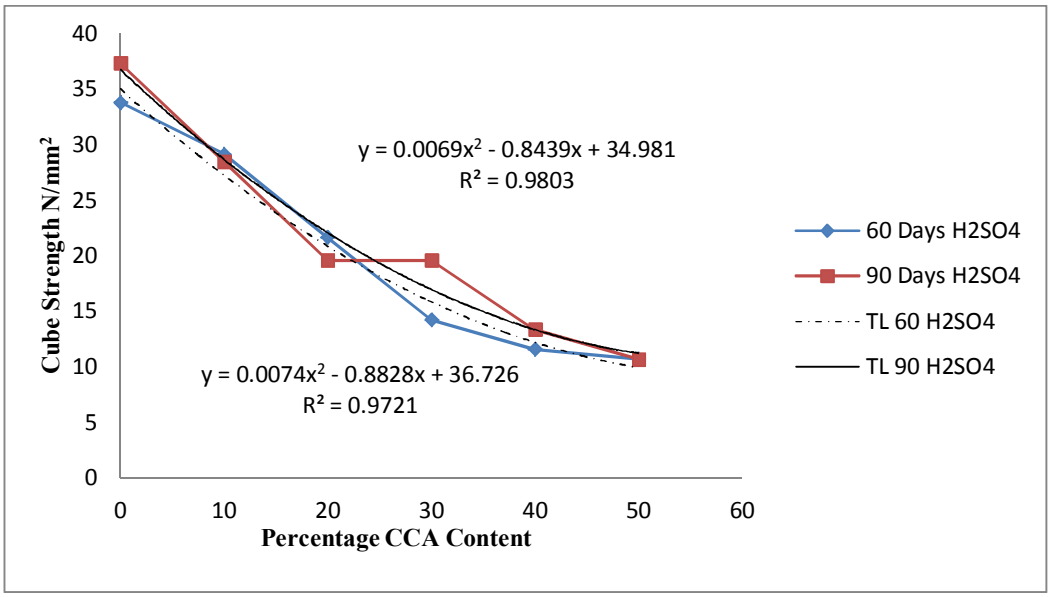


Figure 4.30: Graph for compressive strength of concrete with varying percentages of CCA content at 60 and 90 day curing period in 10% Sulphuric acid solution.

10%H_2SO_4 Solution	60 Days	$y = 0.006x^2 - 0.843x + 34.98$ $R^2 = 0.980$	Computed compressive strength in (N/mm^2) 34.98	Experimental value of compressive strength in (N/mm^2) 33.78
10% H_2SO_4 Solution	90 Days	$y = 0.007x^2 - 0.882x + 36.72$ $R^2 = 0.972$	36.72	37.33

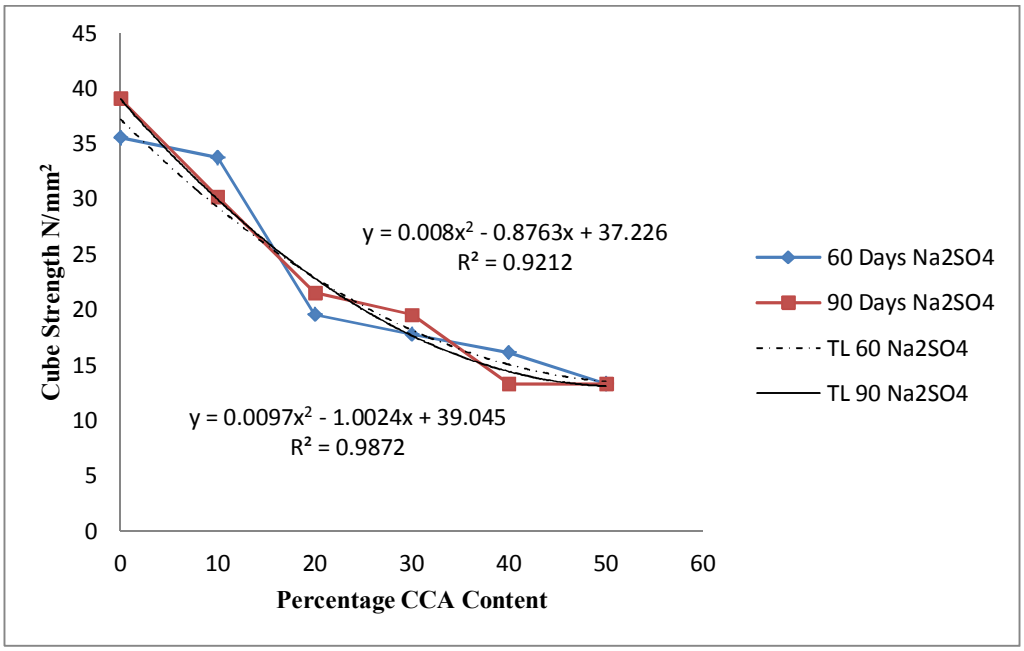


Figure 4.31: Graph for compressive strength of concrete with varying percentages of CCA content at 60 and 90 day curing period in 5% Sodium sulphate solution.

5% Na_2SO_4 Solution	60 Days	$y = 0.008x^2 - 0.876x + 37.22$ $R^2 = 0.921$	Computed compressive strength in (N/mm^2) 37.22	Experimental value of compressive strength in (N/mm^2) 35.56
5% Na_2SO_4 Solution	90 Days	$y = 0.009x^2 - 1.002x + 39.04$ $R^2 = 0.987$	39.04	39.11

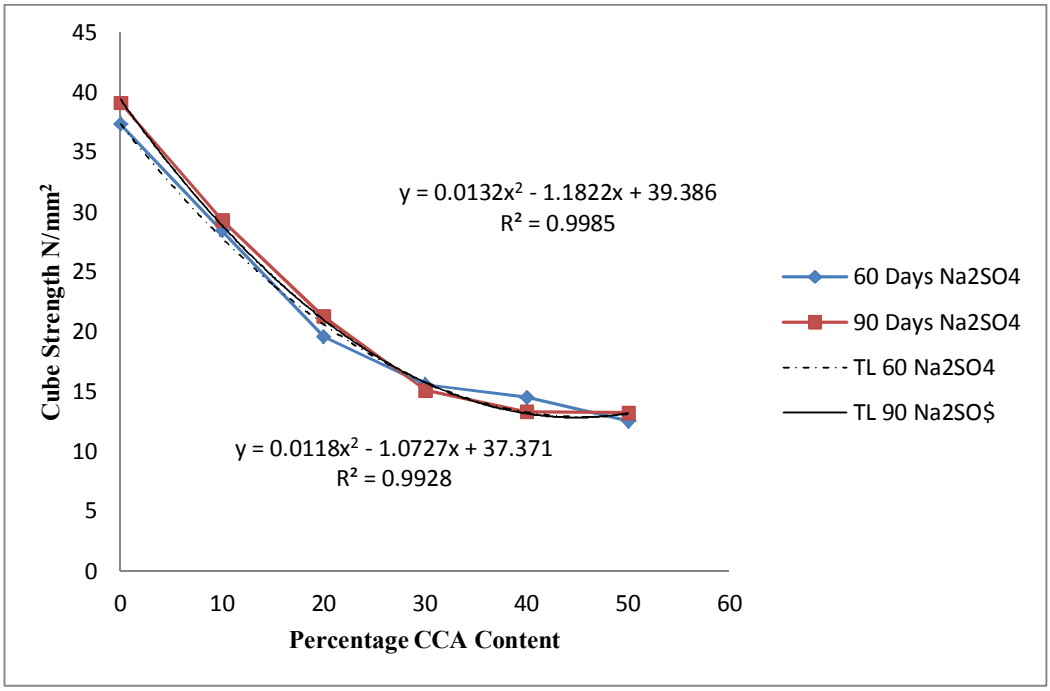


Figure 4.32: Graph for compressive strength of concrete with varying percentages of CCA content at 60 and 90 day curing period in 10% Sodium sulphate solution.

10% Na_2SO_4 Solution	60 Days	$y = 0.013x^2 - 1.182x + 39.38$ $R^2 = 0.9985$	Computed compressive strength in (N/mm^2) 37.37	Experimental value of compressive strength in (N/mm^2) 37.33
10% Na_2SO_4 Solution	90 Days	$y = 0.011x^2 - 1.072x + 37.37$ $R^2 = 0.9928$	39.38	39.11

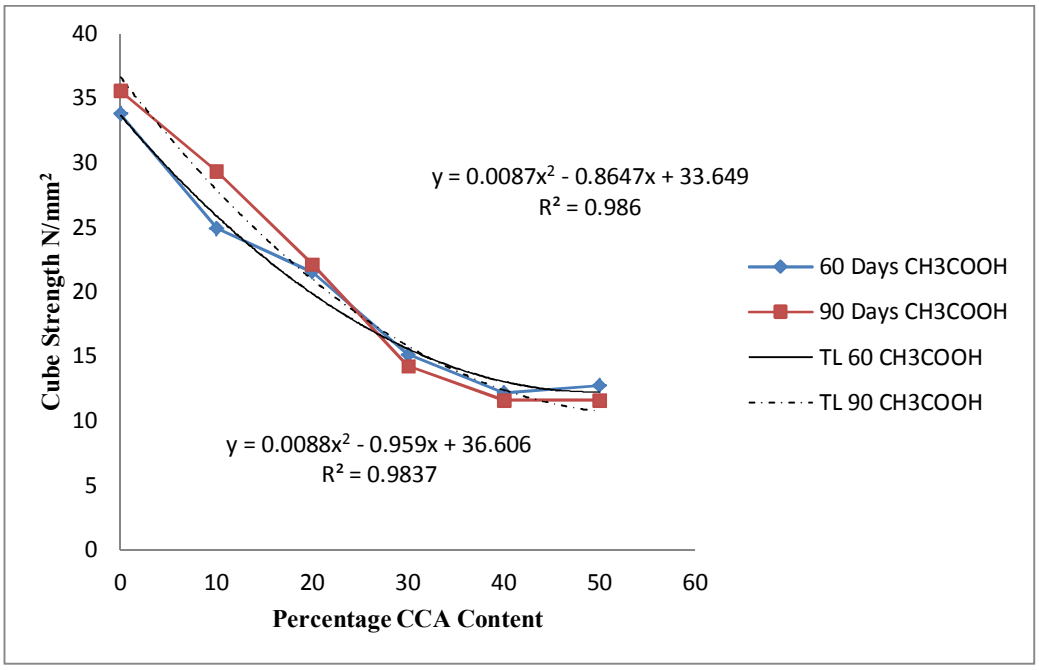


Figure 4.33: Graph for compressive strength of concrete with varying percentages of CCA content at 60 and 90 day curing period in 5% Acetic acid solution.

5% CH_3COOH Solution	60 Days	$y = 0.008x^2 - 0.864x + 33.64$ $R^2 = 0.986$	Computed compressive strength in (N/mm^2) 33.64	Experimental value of compressive strength in (N/mm^2) 33.78
5% CH_3COOH Solution	90 Days	$y = 0.008x^2 - 0.959x + 36.60$ $R^2 = 0.983$	36.60	35.56

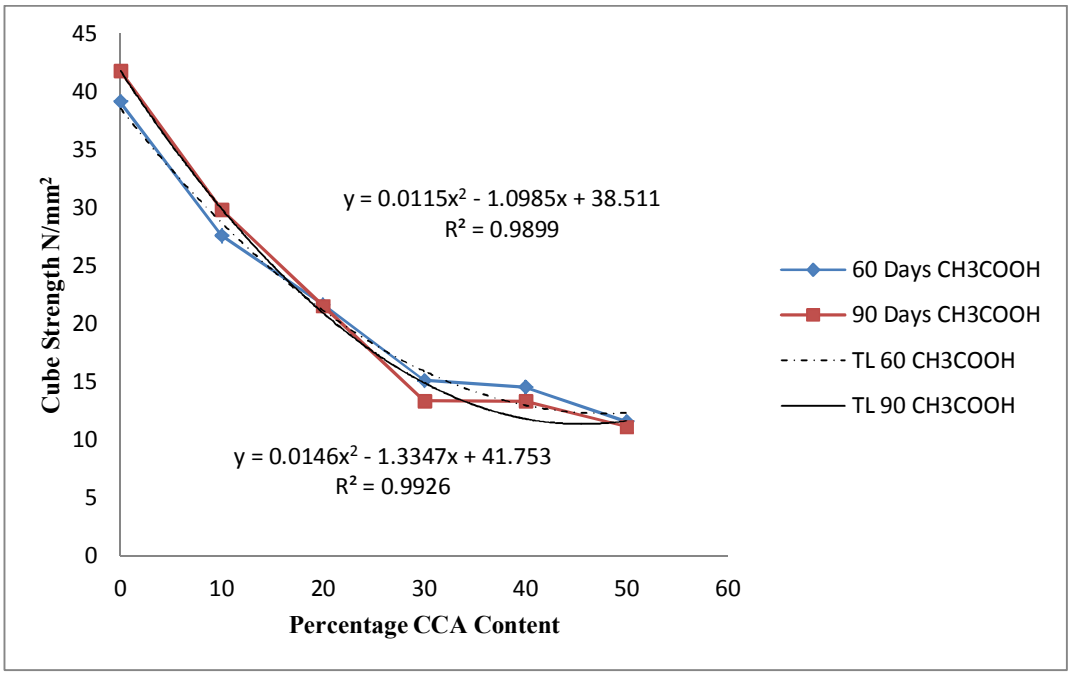


Figure 4.34: Graph for compressive strength of concrete with varying percentages of CCA content at 60 and 90 day curing period in 10% Acetic acid solution.

10% CH_3COOH Solution	60 Days	$y = 0.011x^2 - 1.098x + 38.51$ $R^2 = 0.989$	Computed compressive strength in (N/mm^2) 38.51	Experimental value of compressive strength in (N/mm^2) 39.11
10% CH_3COOH Solution	90 Days	$y = 0.014x^2 - 1.334x + 41.75$ $R^2 = 0.992$	41.75	41.78

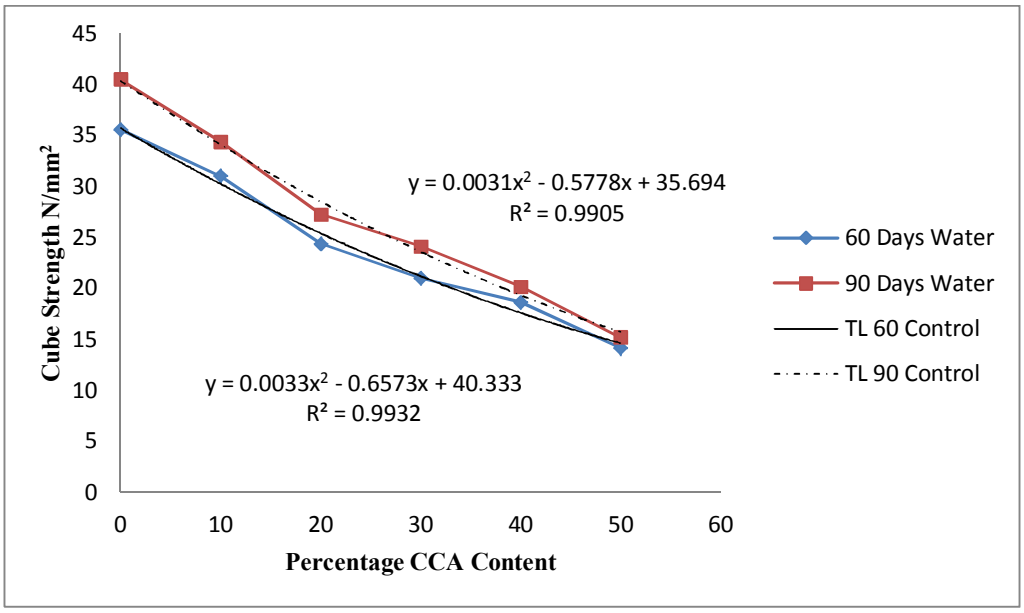


Figure 4.35: Graph for compressive strength of concrete with varying percentages of CCA content at 60 and 90 day curing period in water

Control (Water)	60 Days	$y = 0.003x^2 - 0.577x + 35.69$ $R^2 = 0.990$	Computed compressive strength at in (N/mm^2) 35.69	Experimental value of compressive strength in (N/mm^2) 35.56
Control (Water)	90 Days	$y = 0.003x^2 - 0.657x + 40.33$ $R^2 = 0.993$	40.33	40.50

The graphs in figures 4.29 to 4.35 show plotted experimental values for compressive strength of cube specimens cured in different chemical solutions for 60 and 90 days. Also plotted on the same graph are trend lines of the actual observed experimental values. Regression models generated from the trend lines generated equations for each plot and this are also presented in the plot area.

A careful study of the plotted experimental values and the trend lines revealed that they are in close agreement. The coefficients of correlation for each plot have been

determined for 60 and 90 days curing periods. 28 days compressive strength was computed from the equations and these values are compared with actual observed experimental values in tables presented directly below the plots. The computed values from the regression equations closely agree with the experimental values shown in tables 4.4 to 4.5. A summary of the results for the average compressive for specimen cured in different chemical solutions is presented in table 4.4 below. The results of values computed from regression equations are presented table 4.5 for comparison purpose.

Table 4.2: Computed values for average cube strength from regression equations for 60 and 90 days curing period

	Age/ Days	Avrage Crushing Strength of Concrete N/mm^2 Percentage Ash Replacement					
		0	10	20	30	40	50
5% H_2SO_4	60	31.08	25.45	20.62	16.59	13.36	10.93
	90	34.24	27.4	21.56	16.72	12.88	10.04
10% H_2SO_4	60	34.98	27.15	20.52	15.09	10.86	7.83
	90	36.72	28.60	21.88	16.56	12.64	10.12
5% Na_2SO_4	60	37.22	29.26	22.9	18.14	14.98	13.42
	90	39.04	29.92	22.6	17.08	13.36	11.44
10% Na_2SO_4	60	37.37	27.75	20.33	15.11	12.09	11.27
	90	39.38	28.86	20.94	15.62	12.9	12.78
5% CH_3COOH	60	33.64	25.8	19.56	14.92	11.88	10.44
	90	36.60	27.81	20.62	15.03	11.04	8.65
10% CH_3COOH	60	38.51	28.63	20.95	15.47	12.19	11.11
	90	41.75	29.81	20.67	14.33	10.79	10.05
WATER	60	35.69	30.22	25.35	21.08	17.41	14.34
	90	40.33	34.06	28.39	23.32	18.85	14.98

Table 4.3: Experimental results for average compressive strength for cube specimens with varying percentage CCA content cured in different chemical media

		Avrage Crushing Strength of Concrete N/mm^2					
	Age/ Days	Percentage Ash Replacement					
		0	10	20	30	40	50
5% H_2SO_4	60	31.25	24.89	21.52	15.57	14.1	10.7
	90	33.78	28.56	21.25	16.89	14.1	11.56
10% H_2SO_4	60	33.78	29.11	21.62	14.22	11.56	10.7
	90	37.33	28.44	19.57	19.56	13.33	10.67
5% Na_2SO_4	60	35.56	33.78	19.58	17.78	16.15	13.33
	90	39.11	30.22	21.56	19.56	13.33	13.33
10% Na_2SO_4	60	37.33	28.44	19.58	15.57	14.5	12.54
	90	39.11	29.33	21.25	15.11	13.33	13.25
5% CH_3COOH	60	33.78	24.89	21.52	15.11	12.15	12.7
	90	35.56	29.33	22.1	14.22	11.56	11.56
10% CH_3COOH	60	39.11	27.56	21.63	15.11	14.5	11.56
	90	41.78	29.78	21.52	13.33	13.3	11.11
WATER	60	35.56	31.00	24.35	21.00	18.62	14.14
	90	40.50	34.35	27.25	24.10	20.15	15.17

The results obtained from the experiment carried out in chapter three have been presented and discussed in this chapter. The behaviour of cement modified with CCA (up to 50% replacement of CCA with cement) and the results have been compared with code requirements and standard practice.

Results obtained for experiments on CCA modified cement showed that they satisfied code requirements for consistency, setting time, and soundness. Concrete containing different proportions (10% to 50%) of CCA were tested to investigate the effect of CCA on concrete. The results obtained were compared to code requirements and presented. Samples of concrete containing CCA were cured in different chemical solutions and the effect of the solutions on specimen was investigated and reported.

Finally regression models of the behaviour of CCA modified concrete cured in different chemical solutions were presented in the form of equations and the results were compared to results obtained from tests carried out in the laboratory.

Discussions in this chapter have shown that although the compressive strength of Corn Cob Ash Modified concrete is lower than for concrete with no CCA, concrete containing Corn Cob Ash are still capable of developing strength that meet the requirements of the codes. After 60 days of curing the concretes containing 20 % of CCA gained strength higher than 30 N/mm^2. Density of CCA modified concrete was less than for concrete containing no CCA but it was not less the value recommended for the mix design used of $2300kg/m^3$.

Statistical methods were used to generate regression models and results were compared to experimental results obtained from the laboratory. Results obtained from regression models compared favourably with results obtained from experiments in the laboratory.

CHAPTER FIVE

CONCLUSION AND RECOMENDATION

5.1 Conclusions

This project covered all the processes from primarily stages of concrete mix design up to the analysis of data obtained. The following conclusions can be drawn from this study:

1. Using the ASTM C618 for classifying pozzolanas, Corn cob ash was classified as a pozzolan in class F.
2. CCA contains calcium oxide, silicon oxide, aluminum oxide and iron oxide.
3. The amount of water required to reach consistency increases with increasing amount of CCA added to the cement paste. This behaviour is similar to that of a retarder.
4. Increase in the percentage of CCA in CCA-cement mortar decreases expansion of the mix.
5. Mortar samples containing up to 40% CCA had expansion not exceeding 10 mm and this satisfied the code requirements BS 4550 (1983), NIS 447(2003).
6. As the percentage of CCA increased in the cement mortar, initial and final setting times increased. The initial and final setting times of mortar samples containing up to 40% CCA satisfied the requirements of BS 12 (1978).
7. Concrete containing CCA generally showed a decrease in bulk density with age of curing. The curves of density against age showed a sharp drop at age 7 days, the decrease after age 7 days was steady.
8. Density of concrete containing CCA decreases as the proportion of CCA increases in the concrete mix.
9. Curves of compressive strength against age for concrete containing CCA are parabolic in nature and this conforms to curves described in BS 8110 (1985). The rate of increase

in compressive strength of CCA concrete with age is rapid in the first seven days and then increases at a diminishing rate.

10. Compressive strength of CCA concrete decreases as the proportion of CCA in the in the concrete increases. Concrete produced without CCA (0% CCA) had a higher compressive strength than concrete containing CCA.
11. As the percentage of CCA content in the concrete increases, the compressive strength decreases.
12. Durability test revealed that as the proportion of CCA in concrete increased the amount of weight loss in acid solutions also increased.
13. Visual inspection of samples cured in 5% and 10% chemical solution, showed that as the percentage CCA content increases, the surface deterioration increases for the same acid concentration.
14. Strength of cubes was consistently higher after 90 day curing period both in 5% and 10% chemical solutions. This showed that pozzolana reaction with lime and cement hydration continued even in the presence of the aggressive media. For the concrete containing CCA cured in Chemical solution, the 90days compressive strength was higher than the compressive strength at 60 days.
15. For samples with the same percentage CCA content, cubes cured in water had a higher strength at the same age than cubes cured in acid solutions,
16. CCA/Cement specimens cured in sodium sulphate solution had higher residual compressive strengths than those for acetic acid and Sulphuric acid. CCA/Cement specimen cured Sulphuric acid solution had the least residual compressive strengths for the same age and CCA content.
17. The loss in compressive strength of CCA concrete cubes at 60 days was lower than that for 90 days curing period in the same solution with the same concentration.

18. Regression models computing the compressive strength of CCA modified concrete cured in different chemical solutions were presented in the form of equations and the results were compared favorably with values obtained from tests carried out in the laboratory. The equation are;

1. 5% H_2SO_4 Solution at 60 days; $y = 0.004x^2 - 0.603x + 31.08$ $R^2 = 0.990$

2. 5% H_2SO_4 Solution at 90 days; $y = 0.005x^2 - 0.734x + 34.24$ $R^2 = 0.994$

3. 10%H_2SO_4 Solution at 60days; $y = 0.006x^2 - 0.843x + 34.98$

$R^2 = 0.980$

4. 10%H_2SO_4 Solution at 90 days; $y = 0.007x^2 - 0.882x + 36.72$

$R^2 = 0.972$

5. 5% Na_2SO_4 Solution at 60 days; $y = 0.008x^2 - 0.876x + 37.22$

$R^2 = 0.921$

6. 5% Na_2SO_4 Solution at 90 days; $y = 0.009x^2 - 1.002x + 39.04$

$R^2 = 0.987$

7. 10% Na_2SO_4 Solution at 60 days; $y = 0.013x^2 - 1.182x + 39.38$

$R^2 = 0.9985$

8. 10% Na_2SO_4 Solution at 90 days; $y = 0.011x^2 - 1.072x + 37.37$

$R^2 = 0.9928$

9. 5% CH_3COOH Solution at 60 days; $y = 0.008x^2 - 0.864x + 33.64$

$R^2 = 0.986$

10. 5% CH_3COOH solution at 90 days; $y = 0.008x^2 - 0.959x + 36.60$

$R^2 = 0.983$

11. 10% CH_3COOH Solution at 60 days; $y = 0.011x^2 - 1.098x + 38.51$

$R^2 = 0.989$

12. 10% CH_3COOH Solution at 90 days; $y = 0.014x^2 - 1.334x + 41.75$

$R^2 = 0.992$

Where y is the computed compressive strength and x is the percentage CCA content.

5.2 Recommendations

Based on the results of this study, the following recommendations are made:

1) Standardization of the use of CCA pozzolana in concrete should be carried.

2) The use of CCA as a low cost binder in blended cement should be investigated.

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APPENDIX 1:

Table A1: Mix Design Results for Grade 30 Concrete

The Aspired strength required G30	$35N/mm^2$
The slump (maximum)	50mm
Maximum size of Aggregate 19mm	19mm
Bulk density of Aggregate	$1710Kg/m^3$
Specific gravity of Aggregate	2,567
Finess modulus of fine Aggregate	2,705
Specific gravity of Fine Aggregate	2,549
Water Requirement (Table 10.16 (a) and 10.16 (b))	$\frac{200 \times 92}{100} = 184Kg/m^3$
Stardard Specific gravity of Cement	3.15
The entrapped air content	2%
Water Cement Ratio (Table 10.8(a))	0.50
Hence,the cement content	$\frac{184}{0.50} = 368Kg/m^3$
Bulk Volume of Coarse Aggregate per unit volume of concrete (Table 10.17)	0.63
Hence, the weight of Coarse Aggregate per cubic meter of concrete	1710 x 0.63 = 1077Kg
The Absolute volume of mix ingredient per cubic meter of concrete are:-	
Cement	$\frac{368}{3.15 \times 1000} = 0.117m^3$
Water	$\frac{184}{1000} = 0.184m^3$
Coarse Aggregate	$\frac{1077}{2.567 \times 1000} = 0.420m^3$
Entrapped Air	$0.02 \times 1 = 0.020m^3$
Total Volume	$0.741m^3$
Hence the volume of Fine Aggregate required	$1 - 0.741m^3 = 0.259m^3$
The corresponding weight	0.259 x 2.549 x 1000 = 660Kg
The weight of material per cubic meter of concrete are:-	
Cement	368Kg
Water	184Kg
Fine	660Kg
Coarse	1077Kg
Total:	2289Kg
Hence, the density of concrete	$2300 Kg/m^3$

APPENDIX 2:

Table A2: Mix design for CCA-Concrete cube tests. (Weights are for $1m^3$ of concrete)

Percentage CCA	Portland Cement	CCA	Water	Fine Aggregate	Coarse Aggregate
0 %	368.00 kg	0 kg	3.73 kg	660 kg	1077 kg
10 %	331.20 kg	36.80 kg	3.73 kg	660 kg	1077 kg
20 %	294,40 kg	73.60 kg	3.73 kg	660 kg	1077 kg
30 %	257.60 kg	110.40 kg	3.73 kg	660 kg	1077 kg
40 %	220.80 kg	147.20 kg	3.73 kg	660 kg	1077 kg
50 %	184.00 kg	184.00 kg	3.73 kg	660 kg	1077 kg

APPENDIX 3: (Photographic Plates Showing Extent of Deterioration of Concrete Cured In Different Acidic Media)



Plate A_{3-1}: Control test cube in 5% H_2SO_4 Solution



Plate A_{3-2}: 10% CCA / Cement Replacement in 5% H_2SO_4 Solution



Plate A_{3-3}: 20% CCA / Cement Replacement in 5% H_2SO_4 Solution



Plate A_{3-4}: 30% CCA / Cement Replacement in 5% H_2SO_4 Solution



Plate A_{3-5}: 40% CCA / Cement Replacement in 5% H_2SO_4 Solution



Plate A_{3-6}: 50% CCA / Cement Replacement in 5% H_2SO_4 Solution



Plate A_{3-7}: Control test cube in in 10% $_{H2SO4}$ Solution



Plate A_{3-8}: 10% CCA / Cement Replacement. in 10% H_2SO_4 Solution



Plate A_{3-9}: 20% CCA / Cement Replacement. in 10% H_2SO_4 Solution



Plate A_{3-10}: 30% CCA / Cement Replacement. in 10% H_2SO_4 Solution



Plate A_{3-11}: 40% CCA / Cement Replacement. in 10% H_2SO_4 Solution



Plate A_{3-12}: 50% CCA / Cement Replacement. in 10% H_2SO_4 Solution

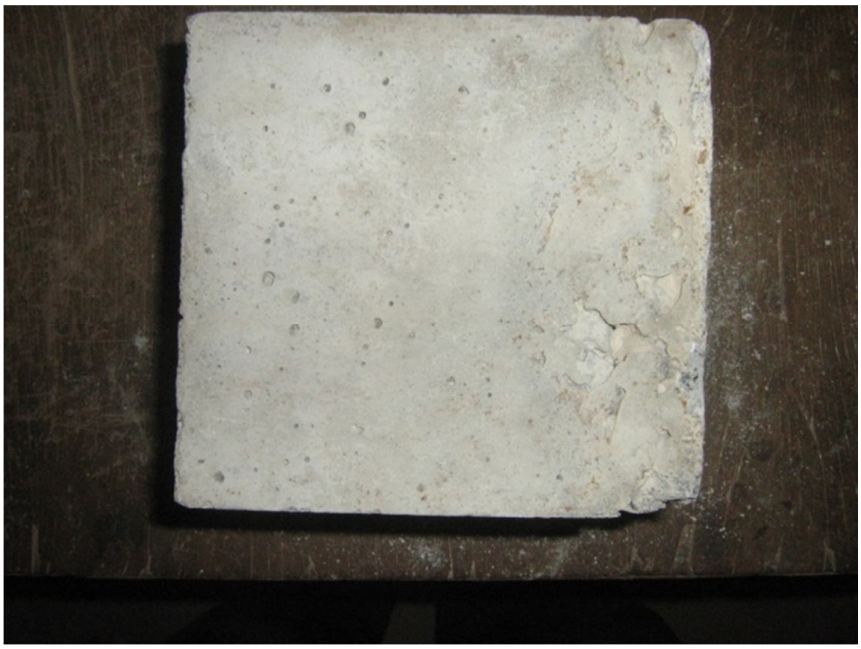


Plate A_{3-13}: Control test cube in in 5% Na_2SO_4 Solution



Plate A_{3-14}: 10% CCA / Cement Replacement in 5% Na_2SO_4 Solution



Plate A_{3-15}: 20% CCA / Cement Replacement in 5% Na_2SO_4 Solution



Plate A_{3-16}: 30% CCA / Cement Replacement in 5% Na_2SO_4 Solution



Plate A_{3-17}: 40% CCA / Cement Replacement in 5% Na_2SO_4 Solution



Plate A_{3-18}: 50% CCA / Cement Replacement in 5% Na_2SO_4 Solution

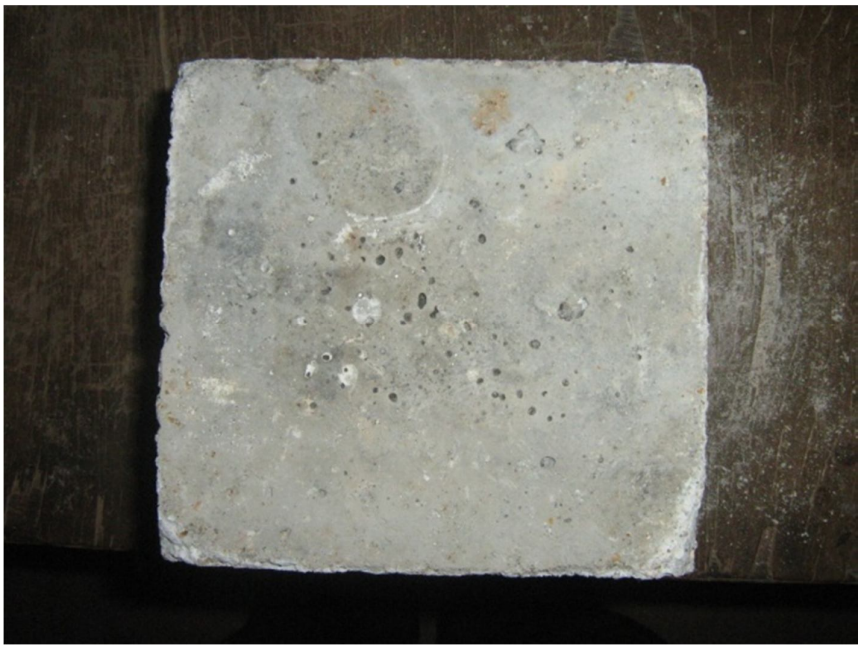


Plate A_{3-19}: Control test cube in in 10% Na_2SO_4 Solution

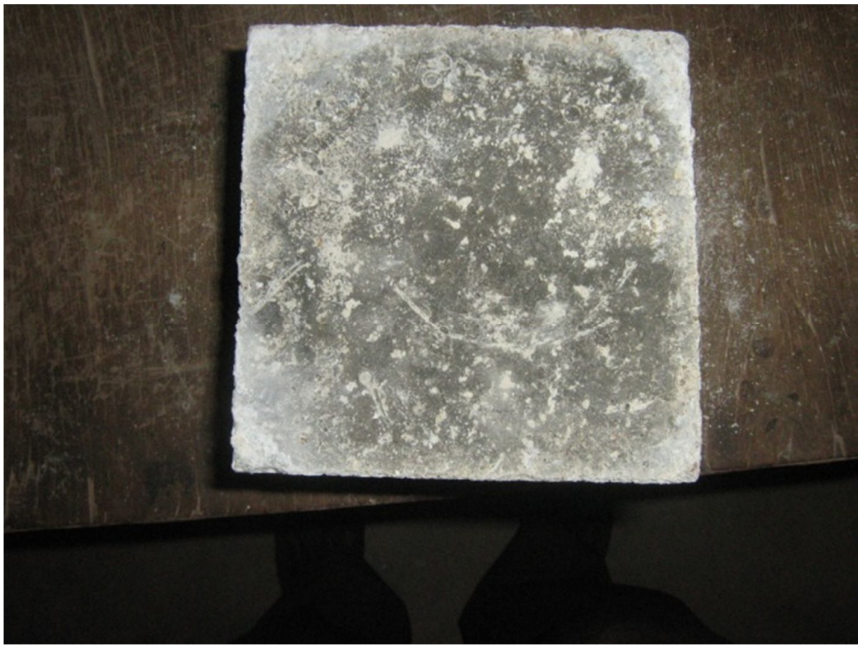


Plate A_{3-20}: 10% CCA / Cement Replacement in 10% Na_2SO_4 Solution



Plate A_{3-21}: 20% CCA / Cement Replacement in 10% Na_2SO_4 Solution



Plate A_{3-22}: 30% CCA / Cement Replacement in 10% Na_2SO_4 Solution



Plate A_{3-23}: 40% CCA / Cement Replacement in 10% Na_2SO_4 Solution



Plate A_{3-24}: 50% CCA / Cement Replacement in 10% Na_2SO_4 Solution



Plate A_{3-25}: Control test cube in in 10% CH_3COOH Solution



Plate A_{3-26}: 10% CCA / Cement Replacement in 10% CH_3COOH Solution



Plate A_{3-27}: 20% CCA / Cement Replacement in 10% CH_3COOH Solution



Plate A_{3-28}: 30% CCA / Cement Replacement in 10% CH_3COOH Solution



Plate A_{3-29}: 40% CCA / Cement Replacement in 10% CH_3COOH Solution



Plate A_{3-30}: 50% CCA / Cement Replacement in 10% CH_3COOH Solution



Plate A_{3-31}: Control test cube in in 5% CH_3COOH Solution



Plate A_{3-32}: 10% CCA / Cement Replacement in 5% CH_3COOH Solution



Plate A_{3-33}: 20% CCA / Cement Replacement in 5% CH_3COOH Solution



Plate A_{3-34}: 30% CCA / Cement Replacement in 5% CH_3COOH Solution



Plate A_{3-35}: 40% CCA / Cement Replacement in 5% CH_3COOH Solution



Plate A_{3-36}: 50% CCA / Cement Replacement in 5% CH_3COOH Solution