Title of Research

The effect of various particle size fractions of fly ash additions on the properties and performance of oil well cements

MSc (50/50)

Prepared by

Gladmore Rongai

Student Number: 1587360

Submitted to

A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in fulfilment of the requirements for the degree of Master of Science in Chemical Engineering (Petroleum Engineering).

Supervisor(s): Dr Diakanua Nkazi

November 2019

DECLARATION

I declare that this dissertation is my own unaided work. It is submitted for the Degree of Master of Science in Chemical Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

………………………………………………………………………………………

(Signature of Candidate)………**08**…day of …**November**…**2019**……

ABSTRACT

Fly ash as supplementary cementitious materials had reduced the total price of Portland cement and has reduced the greenhouse gas emissions resulting in a sustainable "green" concrete. This study investigates the effect of various particle size fractions of fly ash as additive to cement in various amount on the properties and performance of oil well cements. An investigation on the effects of the different particle size and the various compositions was made. The fly ash were separated using sieves laid on top of the other and were allowed to vibrate allowing sieving of the fly ash. Various sieve sizes were used including 25um, 38um, 45um, 53um, 68um, 75um as well as 90um respectively. The retained fly ashes within the sieves were tested for performance when mixed at 0.35 water to cement ratio.

The fly ash - cement slurries were tested for their shear stress and rate, compression strength, as well as water loss for a specific particle size and in different compositions. Graphs were plotted to show the different performance of cement slurries at different particle size composition against shear rate and shear stress. Experiments were carried out to determine the performance of the different particle size composition on the compressive strength and water loss. AAS was also used to determine the chemical composition of the fly ash and cement.

Higher and low compression strength were observed for 38um and 75um particle size of the fly ash, respectively. Low fly ash content (10%) showed better strength compared to 40 %. Rheology test showed that fly ash - cement slurries followed the Bingham plastic model. An increase in fly ash content (from 10% to 70%) decreases the apparent viscosity from 596.59 and 394.17Pa. Results also showed that higher content fly ash lowered the yield stress of cement mixture. Finally, highest rate of water loss was recorded for low fly ash content (10 %).

DEDICATION

My family Genenia, Gregory, Gabriel, Georgina and Gloria have been a source of my stronghold and really supported me all the way through. Gratitude goes to my wife Noreen Chiyaka for her unwavering support and dedication towards success and my lifetime friend Dr Joshua Gorimbo for his everlasting desire for us to build reputable carriers.

ACKNOWLEDGEMENTS

Thanks are due to my supervisor, Dr Diakanua Nkazi for his help, useful criticisms and inspirational support during the experiments, writing and compilation of this dissertation. His enthusiasm, expertise and unending determination for results have really inspired me to sail through this journey up to the destination.

Table of Contents

List of Tables

List of Figure

List of Abbreviations

15F85C	15% fly ash 85% cement
35F65C	35% fly ash and 65%cement
65F35C	65% fly ash and 35% cement
AAS	Atomic Absorption Spectroscopy
ASTM	American Society of Testing Materials
(C-S-H)	Calcium-silicate hydrates
GGBFS	Ground granulated blast furnace slag)
mg/m^3	Milligrams per cubic meter
Rpm	Rounds per minute
SCM	Supplementary Cementitious Material
w/c	Water to cement ratio

CHAPTER 1
Introduction

Consumption of petroleum products has been increasing tremendously with the world consuming more than 93,500,000 barrels per day as per CIA World Factbook (2017). Increase in consumption of fuel puts pressure on the establishment of productive wells. However, these must be established in a sustainable way to avoid pollution and environmental contamination. Designing of oil wells and cementing must be done in a way that promotes optimization of well production. Oil spills such as the recent Gulf of Mexico deep-water horizon oil spill are some of the potential hazards of oil well cementing. Cementing of oil wells is done deep in the offshore at depths amounting to 1600m or more exposing the well to very high temperatures and pressures (Gulliot, 2007). The world is in need of more crude oil, hence this demand cannot be fulfilled without going deep into the offshore, extract the oil and circumvent the challenges face. This has made cementing of oil wells a high priority in the exploration and drilling industry.

Cement has been the most consumed commodity in the world because of its use in construction. It is easy to use and has suitable properties, thus the demand for cement has increased over the years. Cement production is quite expensive and hazardous to the environment. During the production of Portland cement, a tone of carbon dioxide is emitted into the atmosphere due to the redox reaction of limestone to lime and carbon dioxide (Bouzouba, 2005).

The use of fly ash supplementary cementitious materials (SCM) in place of Portland cement as a raw material in the construction industry has reduced the greenhouse gas emissions resulting in a sustainable “green” concrete. The supplementary cementitious materials replace a certain percentage of the Portland cement.

When fly ash and Portland cement are mixed together, it contributes to the properties of the hardened slurry in a reaction known as the “hydraulic activity. Pozzolan is a material that contains silica and aluminum which reacts with calcium hydroxide in the presence of moisture at ambient temperatures to exude cementitious properties (Thomas, 2007).

Bouzouba et al. (2005) 60% of construction companies in Ontario use fly ash with the most commonly used SCM being ground granulate blast furnace slag (GGBFS).

When fly ash is used, the products of hydration of Portland cement in the pozzolanic particles of fly ash combine with calcium and alkali hydroxide, released within the paste's pore structure. The pore spaces of a cured concrete containing fly ash hydrate with cement particles are filled with the reaction products thereby lowering the permeability to aggressive chemicals and moisture (Manmohan and Mehta, 1981).

This project intends to establish the benefits and drawbacks of the addition of fly ash of various particles sizes in different proportions to the use of Portland cement in oil wells.

Some work done on the general effects of the addition of fly ash to Portland cement especially on the chemical constituents and mechanical properties of the resultant fresh cement mixture showing some positive attributes of the fly ash on the concrete. However, there has not been an evaluation of the effects of the added fly ash particle size on the properties (viscosity and compressive strength) and performance of the cement slurry during oil well cementing in oil production, which is what this thesis is going to dwell on.

1.1 Fly ash as carbon dioxide emission reducer

Over the last 100 years, demand for Portland cement has been increased due to the economic development, and industrialization of the world. There is a correlation between demand for Portland cement and air pollution. Increase in Portland cement demand increases air pollution due to the amount of Carbon dioxide produced during the production of cement. Ralane (1983) found out that per every 2 tonnes of Portland cement produced, 1 tonne of carbon dioxide is also produced. This has resulted in an increase in the global warming of the world and resulted in massive air pollution.

The introduction of fly ash as a supplementary cementitious material helps the reduction of the amount of cement demand in the world there by reducing the carbon dioxide emissions. Use of SCM has advantages and disadvantages depending on the chemical composition as well as the total amount and the particle size added to the cement on the rheological and performance of the cement slurry.

With increasing demand for petroleum products, oil well cementing activities become a thing of the day hence the need to use SCMs to reduce the pollutions resulting from increased production of OWC to meet the demand in the industry.

1.2 Research Problem

Infrastructural development is a vital and key activity in the development of a country and is the backbone for the economic activities. Roads, buildings and bridges are pivotal necessities, used to evaluate the economic status of a country. Cement has been at the center of infrastructural development and has become a core construction raw material. This has subsequently increased the demand of cement not only in infrastructure but also in the exploration and extraction of crude oil both inland and offshore.

Crude oil extracted in the deepest parts of the sea for example the Gulf of Mexico were high temperatures and pressure are the greatest challenges for drilling and sustaining a well. Cement is used for the construction of a casing to keep the well from collapsing. It is of paramount importance that the casing be strong and of high pressure resistant. However, the pumping in of the cement slurry has to be easy, energy conservative, this is achievable if the workability, and pumpability of the cement slurry is less laborious. The introduction of fly ash makes this very easy and less energy consumptive because the fly ash in the cement slurry reduces the viscosity, which makes it easy to pump the slurry into the casing.

A. Martini (2008), have indicated that indeed fly ash can be a good substitute for cement. However, it has not been established as to which particle size and cement to fly ash ratio gives the best performance in terms of the rheological properties, which can meet and survive the high-pressure high temperature offshore conditions in the sea.

Despite the excitement, happiness and advancement in theory with which many researchers have reported the effective use of fly ash substitution as SCM. It should be noted that the chemical composition of the fly ash differs from source to source due to the electricity production plant design, as well as the type, source and origin of the coal used as fuel in the electricity generating plant. Fly ash for instance from one electricity generating plant will not necessarily have the same properties as well as chemical composition of fly ash from another plant.

Hence, this study will look at the particle size and chemical composition of a specific fly ash obtained from Secunda refinery and its effect on the resistance and sustainability of oil wells in the offshores.

1.3 Research Questions

In solving the research problem mentioned above the following questions will be answered;

- What is the effect of different particle sizes on the viscosity, shear stress and shear rate measurements on a rheometer?
- What effect does the fly ash composition have on the rheological properties of the fly ash /cement slurry
- What is the effect of different particle sizes on the performance of the resultant slurries on the compressive strength and water loss?

1.4 Research Aims

The aims of this research project are as followed:

1. To establish the effects of fly ash particle size and fly ash to cement ratio at a fixed water/cement ratio of 0.35 on the performance of oil well cement.
2. To establish the resultant effect of the performance of the particle size and fly ash to cement ratio rheological behaviour on the casing of oil well cements.

1.4.1 Objectives

The aim of this project will be achieved through the outlined objectives:

1. Establish the optimum fly ash particle size for oil well cementing
2. Determine the maximum/Minimum fly ash /cement composition of the optimum fly ash particle size for oil well cementing**.**
3. Establish the fly ash cement composition, which retains enough water.
4. Determine the optimum fly ash particle size that best suits oil well cementing properties.

1.4.2 Hypothesis

Is there a relationship between the addition of fly ash in a specific amount of cement to water ratio of 0.35 for a specific fly ash particle size, and the performance of the resultant concrete in oil well cementing properties?

1.5 Scope of Research

The scope of the research encompasses the use of Fly ash produced by Secunda from the electricity generation separating it into different particle sizes and mixing them in different compositions of fly ash /cement ratios. The resultant slurry is then analysed for its rheological and physical properties.

1.6 Dissertation Outline

This dissertation is divided into four chapters, each explaining the different aspects of the experiments carried out. A summary of the chapters is given below.

Chapter 1: Introduction

A brief background of the sustainable replacement of cement with fly ash is given as well as the benefits and possible disadvantages of using fly ash /cement mixtures in concrete construction. An outline of the motivation of the research, research problem, aims and objectives, hypothesis and the scope of the research are also discussed briefly.

Chapter 2: Literature Review

An in-depth explanation into the source, physical properties and chemical composition of the fly ash / cement mixture is given. The effects of supplementing cement with fly ash is thoroughly discussed .A review of previous research involving the use of fly is also presented on a theoretical basis.

Chapter 3: Experimental Apparatus and Methods

This chapter describes the experimental procedure, research methodology and Procedures for the research work. The experimental techniques used in order to determine the rheological properties of the fly ash / cement slurries. Different methods of evaluating the physical properties of the resultant cement slurries and concrete relative to performance in the oil well cement casing.

Chapter 4: Results and discussion

This chapter dwells on the results and discussion associated with the outcome of the rheological measurements as well as the results of the experiments carried out. The experimental data is analyzed using Excel sheet and the extrapolation of graphical representation. From these studies the effects of particle size and fly ash to cement composition on the rheological properties and physical properties of the cement slurry and concrete under investigation was determined.

Chapter 5: Conclusions and Recommendations

This chapter presents a summary of the findings and conclusions of the work performed in this project and recommendations are given for further study.

Lastly the list of referenced material and appendices are given.

CHAPTER 2
Literature Review

Oil Well Cementing is the introduction of cement slurry in the space between the well casing and the mud surrounding the well bore with an intention of preventing the collapsing of the well bore. Josh et al, (1997), introduced the process of oil cementing in the late 1920s. Josh et al (1997) proposed that oil well cementing had a number of benefits which include the following,

- Prevention of mixing of crude oil with water
- Preventing the collapse of the well
- Preventing corrosion of the oil well casing
- Strengthening the casing

Oil well cementing then calls for specific properties of the cement to ensure capability to resist high pressure and temperatures underneath the surface. Thus there must be strict control of the hardened concretes parameters which include the mechanical properties, durability and chemical reactivity. This calls for a special class of cement called oil well cements (OWC) which is specified by the American Petroleum Institute (API) specifications 10A of 2002. There are many additives and substituents used with the OWC in cementing wells including fly ash. These have been added to either improve the followability, stability and performance of the wells or to reduce other disadvantageous properties of the OWC. Research has been carried out to improve the efficiency of oil wells by improving the physical and mechanical properties of OWC slurries. This section discusses the basic concepts involved in oil well cementing, the different types of OWCs, and their chemical and physical properties.

Oil wells can be very deep measuring up to several thousand meters and less than or equal to a meter in diameter (Lafarge, 2009). They can be dug onshore or offshore using a rig. When drilling is finished, the mud is removed and the bore is left open. There are chances that the bore of the well will collapse hence the need to cement with OWC to which ensures strong bonding between the casing and the geographical material surrounding the well. Temperatures within the well may rise to above 500^{o}F and this temperature has to be cooled by the circulation of cooing drilling mud (Orchard, 1962). Pressures amounting to 250MPa can be reached in the well depending on the depth of the well (Joshi et al., 1997). This makes it necessary for the OWC slurries to be pumped in between the well bore and the steel casing to seal off all the geographical strata except those, which have oil and gases. Power et al. (1977) postulates that the OWC is pumped through the annular spacing between the casing and the subterranean bore wall in the well. When pumping the OWC slurry, care is taken not to close the perforations from which the crude oil sips into the bore. This will reduce the productivity of the well if not taken into consideration. When the cementing process is completed, a curing time is allowed for the slurry to harden before completion of work on the well. Figure 2.1 shows a schematic representation of a cemented oil well.

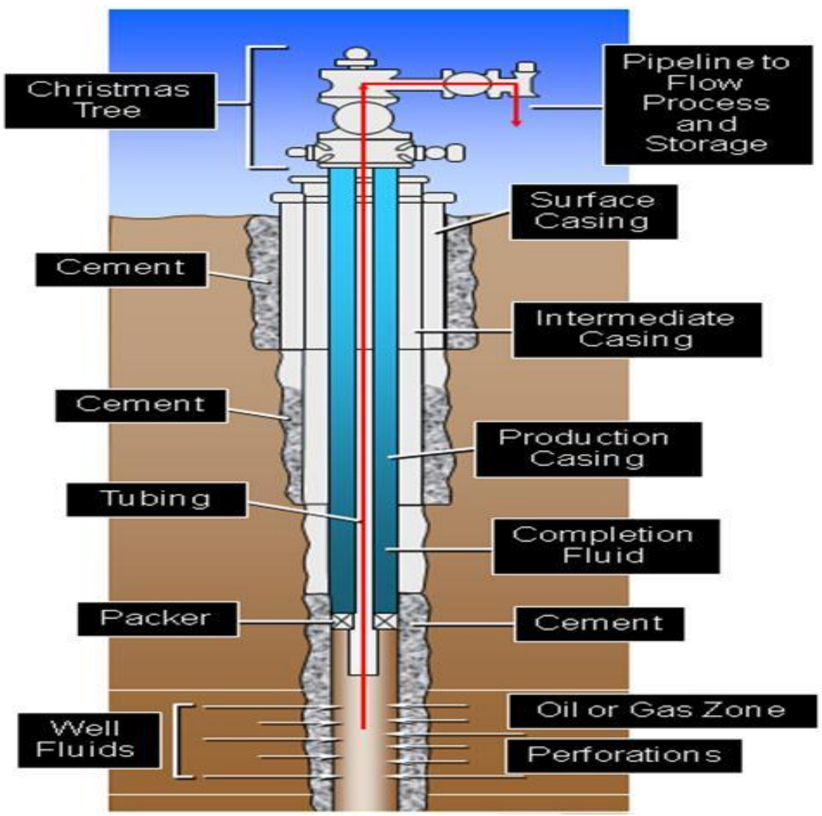


Figure 2. 1: Schematic representation of a cemented oil well

Source: Texas Oil & Gas, (2015)

2.1 Types and Classification of Oil well cements

Productivity of wells is usually influenced by the stability of the well, its capability to reduce contamination and resistance to high temperatures and pressures. These parameters determine the type of OWC that must be used in cementing oil wells. Oil-well cements are made from Portland cement clinker or from blending different types of hydraulic cements.

The Unites States Department of Transportation, (2009), proposed Types I and II Portland cements as the cements that can provide the strength which can withstand the rough conditions exposed to a well. However, Popovics, (1992) proposed that Types I, II and III Portland cements are effective in cementing cases which are 1800m deep.

OWC form the basis for making slurry mix for cementing oil wells. There are standards for the development of OWC and these have been made international according to the API Standardization committee, (1937). API Specification 10A, (2002) stipulated the API specifications for Materials and Testing for well cements which classified OWC into grades based on their C_3A (Tricalcium Aluminate) content, Moderate Sulphate Resistant (MRS) and High Sulphate Resistant (HRS). These classes distinguish the OWC according to the depth, pressure and temperature. Lafarge, (2009) proposed that the commonly used OWC classes are Class A, Class G and Class H. Lafarge, (2002) further classified them according to the depth of application with Class A being used for less demanding well conditions, while Class G and H are used specifically for deeper, hotter and very high pressure conditions. These classes are also distinguished according to their chemical compositions, with most of the OWC having a lower C_3A content, being coarsely ground, containing friction-reducing additives in addition to gypsum (Popovics, 1992). The following table shows the chemical and physical properties of OWC class G and class H.

Table 2. 1: Chemical and physical composition specifications

Source: API Specification 10A (2002) Class G and Class H.

Chemical Component (%)	**API Specification 10A, (2002)**
Magnesium oxide (MgO)	≤6.0
Sulphur Trioxide (SO_3)	≤3.0
Loss on Ignition	Loss on Ignition ≤3.0
Insoluble Residue	Insoluble Residue ≤0.75
C_3S (For MSR)	48-58
C_3S (For HSR)	48-65
C_3A (For MSR)	≤8.0
C_3A (For MSR)	≤3.0
C_4 AF+2 C_3A	≤24
Equivalent Alkali (Na_2O)	≤0.75

Physical Properties	**API Specification 10A, (2002)**
Maximum free fluid content, %	5.9
Thickening Time (Schedule 5: 52°C and 35.6 MPa)	≤120 minutes
Compressive strength at 8 hours @ 38 C and atmospheric pressure MPa	2.1
Compressive strength at 8 hours @ 60 C and atmospheric pressure	10.3
Soundness (automotive expansion), %	≤0.8

According to the API Specification 10A, (2002), class G and H have the same chemical compositions but only differ in the surface area in which class H is much coarser than class G cement. These two OWC are the most commonly used OWC. This research will look into the mixing of OWC with SCM to find the best combination in terms of composition of fly ash and the particle sizes in determining the optimum resultant slurry that can improve the performance of OWC leading to improved well production.

The source of fly ash that is used, as a supplementary cementitious material to blend with cement, is a byproduct of burning coal in electricity production plants. When the coal is ignited in the furnace, most of the volatile matter and carbon in the coal are exposed to oxygen hence combustion. During the combustion process, the mineral impurities of coal such as quartz, clay and shale fuse in in the air and transported from the combustion chamber by gases from the exhaust chamber. At the end of this process, the materials fused at high temperature forms spherical solid glassy particles when cooled. The ash is a finely divided powder resembling Portland cement. The finely divided ash contains varying amounts of calcium, which reacts with the calcium hydroxide when mixed with Portland cement and water thus the reaction produces calcium-aluminate hydrates and calcium-silicate hydrates (C-S-H).

Lafarge, (2002) proposed that the hydrating reactions have advantages to the concrete as they multiply the quantity of the binding phase (C-S-H) and to a lesser extent for the calcium-aluminate hydrates. This significantly improves the strength of the concrete at the expense of the systems permeability.

2.2 Cement composition and its hydration kinetics

Cement is manufactured by the following raw materials lime, silica, alumina and iron oxide.

These oxides interact at very high temperatures in the kiln to form complex compounds. The proportions of these oxides and the complex compounds influence the various properties of cement.

Table 2. 2:Oxide composition limits of ordinary Portland cement

Source: Saha, 2017

Oxide	Percent Content
CaO	60-67
SiO_2	17-25
Al_2O_3	3.0-8.0
Fe_2O_3	0.5-6.0
MgO	0.1-4.0
Alkalis(K_2O,Na_2O)	0.4-1.3
SO_3	1.3-3.0

The quantification and identification of the oxide compounds of cement is based on the Bogue's equations hence they are termed the "Bogue's Compounds". There are four major compounds with greater and relevant significance in cement and these are listed in Table 2.3.

Table 2. 3: Major compounds of cement

Compound	Compound Formulae	Abbreviation
Tricalcium silicate	$3CaO.SiO_2$	C_3S
Dicalcium silicate	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A
Tetracalcium Aluminoferrite	$4CaO.Al_2O_3$	C_4AF

For simplicity's sake abbreviated notations are used and these are as follows, C stands for CaO, S stands for SiO_2, A for Al_2O_3, F for Fe_2O_3 and H for H_2O. The minor oxides namely K_2O and Na_2O are referred to as alkalis oxides.

The alkalis compounds react with silica to produce alkali-silica, which causes swelling under favorable conditions of moisture and temperature .Whilst the Tri-calcium silicate and di-calcium silicate, are involved in strengthening of the cement. Together they constitute 70 to 80 per cent of cement. Addition of gypsum during the process of clinkering leads to the presence of SO_3 in cement analysis. The percentage of MgO in cement comes from Magnesia compounds in raw materials. The purpose of this oxide is to control expansion from its hydration. Availability of lime as CaO beyond the specifications has a direct effect on the cements combination with other compounds. This makes the cement to become unsound. The cement also constitutes insoluble residue, which is non-soluble in hydrochloric acid HCl, and arise

2.1.2 Cement hydration and kinetics

Experimental results have revealed that the four major composites of cement, that are C_3S, C_2S, C_3A and C_4AF have different rates of reaction with water (Al Martini, 2007).C_3A reacts faster, followed by C3S and the other two respectively. Feng et al, (2009) proposed a model which contains the four material constants (k, A_0 ′, n_o and the apparent activation energy E_a). The constants k, A_o ′, n_o are functions of the chemical composition of cement whilst the activation energy depends also on the fineness of cement.

Schindler (2004) proposed an equation for the apparent activation energy, which is as follows

$$E_\alpha\ [J/mole], = 22100 \times (PC3A)^{0.3} \times (PC4AF)^{0.25} \times (Blaine)^{0.35} \qquad (2.1)$$

In which the PC_3A and PC_4AF are Bogue mass fractions of C_3A and C_4AF, respectively. Blaine, which is a measure of the cement fineness, influences the initial reaction rate of cement. Therefore, it is involved in the expression for the parameter A_0, representing the initial chemical affinity of the hydration of cement. Feng et al. (2009), used the following equation to express the constant A_o

$$A_o = \frac{A_o \ x \ Blaine}{350} \tag{2.2}$$

Martin, (2007) postulated that the chemical composition of cement affects both the chemical affinity $A_{\square}$ and the permeability $\eta_{\square}$,. Whereas, the water cement ratio influences only the chemical affinity $A_{\square}$. The following equation shows the relationship between the chemical affinity $A_{\square}$ to the chemical composition of cement and water–cement ratio.

$$A_\alpha \propto \mathrm{K}\ (\frac{A_o}{k\alpha_u}+\alpha)\ (\alpha_u - \alpha) \tag{2.3}$$

In which K and A_o are parameters related to the chemical composition of cement and other factors. A_o is the initial chemical affinity of cement hydration and the effects of $A_{\square}$ and $\eta_{\square}$ are shown through their products. Feng et al. (2009) went on to simplify the model by using an exponential equation to represent the permeability $\eta_{\square}$,

$$\eta_\alpha = \exp(-n\alpha) \tag{2.4}$$

With the above discussion and formulation, Finger et al. (2009), proposed the following mathematical model of hydration kinetics for Portland cement

$$\acute{\alpha} = A_\alpha \eta_\alpha \exp(\frac{E_a}{RT}) \tag{2.5}$$

In which $\acute{\alpha}$ is the cement hydration.

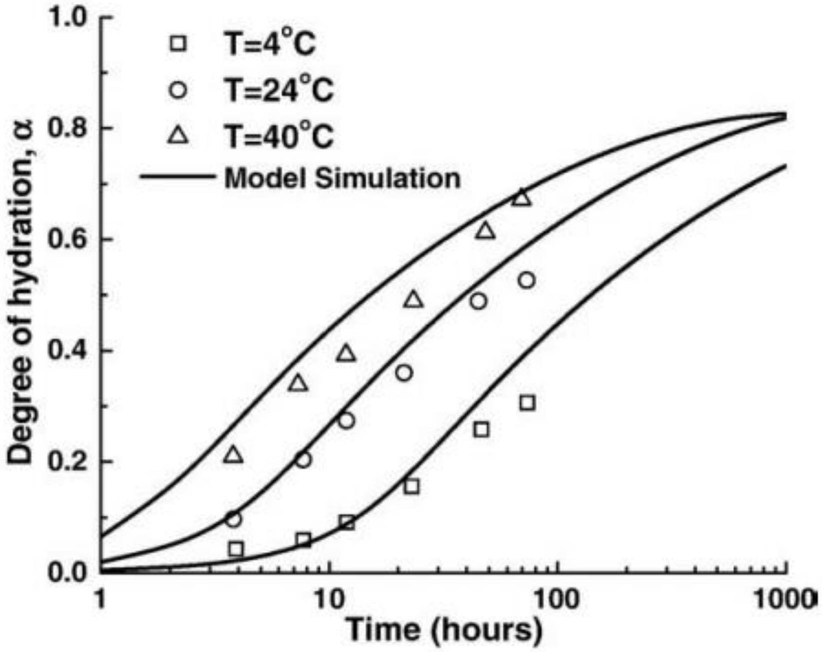


Figure 2. 2: Simulated and measured degree of hydration for cement #A (type I)

(A.K Schindler 2004).

Figure 2.2 indicates that the model simulation shows that there is a relationship between the temperature and degree of hydration. At higher temperatures, the degree of hydration is higher compared to lower temperatures. The chemical shrinkage of cement paste can be calculated. Schindler. (2004) proposed that the chemical shrinkage is approximated as follows,

$$Vchsh = \frac{(1-Vn)x\,\frac{wn}{c}\,x\,\alpha}{Vc+\frac{w}{c}} = \frac{0.25\ x\ 0.25\ x\ \alpha}{0.32+\frac{w}{c}} \tag{2.6}$$

Where V_{chsh} (α) is the chemical shrinkage; v_n (≈0.75 cm3/g) is the specific volume of the chemically bound water, w_n is the mass of the chemically bound water; and v_c (≈0.32 cm3/g) is the specific volume of cement.

The proposed hydration model can be used for the prediction of hydration kinetics, adiabatic temperature change and chemical shrinkage of cement paste.

2.2 Environmental impact of cement

Cement production results in the production of by-products and wastes. Some of which are detrimental to the environment as well as human health. The main pollutions of cement productions are, pollution to the water, air, production of solid waste, noise pollution, ground vibration. Gases from the kiln are also released which pollute the environment and these include, CO_2, N_2, SO_2 and other oxides. The polluting gases are produced in the following two stages

i) Calcinations: During the CaO formation, the carbon dioxide is release together with water because of the very high temperatures.

ii) Fuel combustion: The operation of a kiln requires very high temperatures and these temperatures are realised by combusting fuel, which contains hydrocarbons. The combustion of the fuel then releases CO_2, NO_2, SO_2 and other oxides, which are harmful to the environment.

Table 2. 4: Types of fuels used in Cement production (Shraddha et al, 2014)

Types of fuel	Energy % Share	Country
Electricity	11–14	Canada and India
Coal	33–41	Canada and India
Natural gas	7–64	Canada, Iran and India
Biomass	19	India
Petro-coke	13	Canada

Table 2.4 indicates that cement production consumes a lot of energy thereby depleting sources of energy leading to a generally higher demand of energy in the world. Apart from gases and dust, cement production produces metals, waste water and particulate matter which also have a drastic impact on the environment.

2.2.1 Sulphur Dioxide

Sulphur dioxide is formed from the combustion of fuels containing the Sulphur element. It is present in most of the cement raw materials. Hesham et al. (2012) proposed that SO_2 emissions generated from sulphur in the raw materials are lower than SO2 emissions generated from sulfur in the fuel. Babatunde et al. (2013), proposed that the oxidation of Sulphur in the kiln is as a result of the very high temperatures ranging from 370 ^oC and 420 ^0C. Sulfur dioxide (SO2) is a buy product of thermal decomposition of calcium sulfate in cement production. The sulfur oxides react with water vapor to form sulfuric acids. The sulphuric acids dissolve rain water and are washed away thereby contaminating drinking water and affecting agriculture production by lowering the ph. of the soil. The acid rain also causes respiratory illnesses such as bronchitis (Hendrik et.al 2003).

2.2.2 Nitrogen oxides

These are produced after the combustion of a rotary kiln, and they enter the atmosphere as exit gases. Hesham et al. (2013) proposed that NO_x are formed as a result of thermal oxidation, which happens in the temperature range of 1,200-1,600 °C in which 90% of the nitrogen oxides are produced in the form of nitric acid which causes a variety of health and environmental impacts.

The nitrogen oxide has a family of nitrogen oxides, including nitrogen dioxide, nitric acid, nitrous oxide, nitrates, and nitric oxide. NO_x react with water and other compounds to form various acidic compounds. These acidic compounds impair the water quality of water bodies thereby lowering the ph. of the water. This affects the fauna and flora surviving in the lakes particularly fish. Nitrous oxide is a greenhouse gas and it accumulates in the atmosphere causing a gradual rise in the earth's temperature leading to global warming and climate change. Health wise, Nitrogen dioxide affects body functions such as breathing problems and chronic lung diseases.

2.2.3 Carbon dioxide

Cement industry is a major source of CO2 emission. It is estimated that half of the CO_2 is generated from fuel combustion and the other half originates from the decarbonization of the raw material. Worrell et al. (2001) proposed that the other pollutant in cement production is from the consumption of electricity, based on the assumption that the electricity is generated from fossil fuels. Worrell et al. (2009) also proposed that Carbon dioxide emissions of fuels can be calculated from emission factors of fuels defined by the Inter government Panel on Climate Change (IPCC)

Table 2. 5: CO2 emission per annum in Puttalam Cement Company Limited (PCCL) plant over the period of 1990-2001 due to calcination (Nisa et al, 2004)

Year	Clinker production (tons)	Emission Factor	CO_2 Production (tons)
1990	382370	0.613	234392.81
1991	398875	0.613	244510.38
1992	408925	0.613	250671.03
1993	423455	0.613	259577.92
1994	415380	0.613	254627.94
1995	403210	0.613	247167.73
1996	439190	0.613	269223.4 7
1997	453335	0.613	277894.36
1998	448505	0.613	274933.57
1999	378358	0.613	231933.45
2000	378286	0.613	231889.32
2001	379200	0.613	232449.60

2.2.4 Particulate matters (PM10, PM 2.5)

Sources of particulate matters include quarrying, hauling, crushing, grinding of raw material and clinker, fuel combustion, and cement packing. Particulate matter remains suspended in the air according to Hesham et al, (2012). Dust emission cause reduced visibility and deteriorated air quality. When the dust is washed with rain, it pollutes water bodies. Abribigbola et al, (2014) proposed that particulate emissions are potentially harmful because they contain toxic metals and compound such as lead, chromium, nickel, Barium, mercury and potential radioactive material. These emissions are toxic as it carries carcinogens, mutagens, immunotoxins, and respiratory toxins, neurological.

Table 2. 6: Type of dusts and their sources USEPA, (1995)

Type of Dust	Source
Raw material dust	Quarrying, crushing and handling of raw material
Feed material	dust Feeding, milling, stacking, blending, reclaiming, conveying, and transferring of feed material
Cement kiln dust	Feeding and processing of materials involving countercurrent circulation of hot gases
Clinker dust	Cooling involving air circulation and open-storage of clinker
Cement dust	Feeding, milling, conveying, bagging and loading of cement materials

The main route of entry of dust particles in the body is the respiratory tract or gastrointestinal tract or both by inhalation or swallowing (Manjula et al., 2014). PM can also cause eye and throat irritation, bronchitis, lung damage, increased mortality rates, increased heart ailments.

2.3 Fly Ash

Fly ash is a by-product of the combustion of pulverized coal in an electricity power generating station. It is mainly the combustion residue from the burning zone of the boiler, collected by mechanical and/or electrostatic separators. Fly ash from the combustion of coal in electricity power generating plants became available in significantly larger quantities in the early 1930s.

Davis et al. (1937) proposed that the first results on fly ash containing concrete were published in 1937 by, R. E. Davis and his research associates from the University of California. These results lead to the establishment of early ASTM test methods for quality specifications. According to

ACI 116R, fly ash is “the finely divided residue resulting from the combustion of ground or powdered coal and which is transported from the firebox through the boiler by flue gases.

Figure2. 3: Showing cement and fly ash

During electricity generation, the heavier incombustible material settles at the bottom of the furnace and is known as bottom ash. However, fly ash is a pozzolanic material which is a finely-divided amorphous alumino-silicate compound containing calcium, which when mixed together with the common portland cement and water in a specific water – cement ration, will form a chemical reaction with the calcium hydroxide to produce calcium-silicate hydrates (C-S-H) and calcium-aluminate hydrates.

There are other types of fly ashes with higher amounts of calcium such that when they mix with water in the absence of a calcium-containing compound, they will produce hydrates and these are termed cementitious fly ash. Fly ash which exhibits such pozzolanic reactions are of benefit to the production of concretes in that quantity of cementitious binder (C-S-H) is enhanced when they are added to cements, thereby enhancing the resultant strength of the cement.

Fly ash in concrete makes efficient use of the products of hydration of portland cement: these products include the solutions of calcium and alkali hydroxide, which combine with the pozzolanic particles of fly ash, to form a cementing medium. Fly ash also makes use of the heat generated by hydration of portland cement to initiate its own pozzolanic reactions. Manmohan et al (1981) proposed that cement and fly ash reaction products fill in the spaces between hydrating cement particles, in so doing lowering the permeability of concrete to water and aggressive chemicals such as chlorides. Mielenz. (1983) alluded that the beneficial aspects of fly ash were notable in the construction of large concrete dams. Sizes may run from less than 1 µm (0.00004 in.) to more than 80 µm (0.00315 in.), and density of individual particles from less than 1 mg/m3 (62.4 lb/ft3) hollow spheres to more than 3 Mg/m3 (187 lb/ft3) according to the ACI Committee.

Chindaprasirt (2005), highlighted that the combustion temperatures of approximately 1600 C (2900 F) melts the incombustible minerals in coal such that when they rapidly cool upon leaving the firebox they form spherical particles, which are glassy in structure. The characteristics of these properties is affected by the combusted coal composition, grinding mill efficiency, boiler/burner configuration, and the rate at which the particles cool. Collection of fly ash from the furnace exhaust gases is done using the electrostatic or mechanical precipitators as shown below

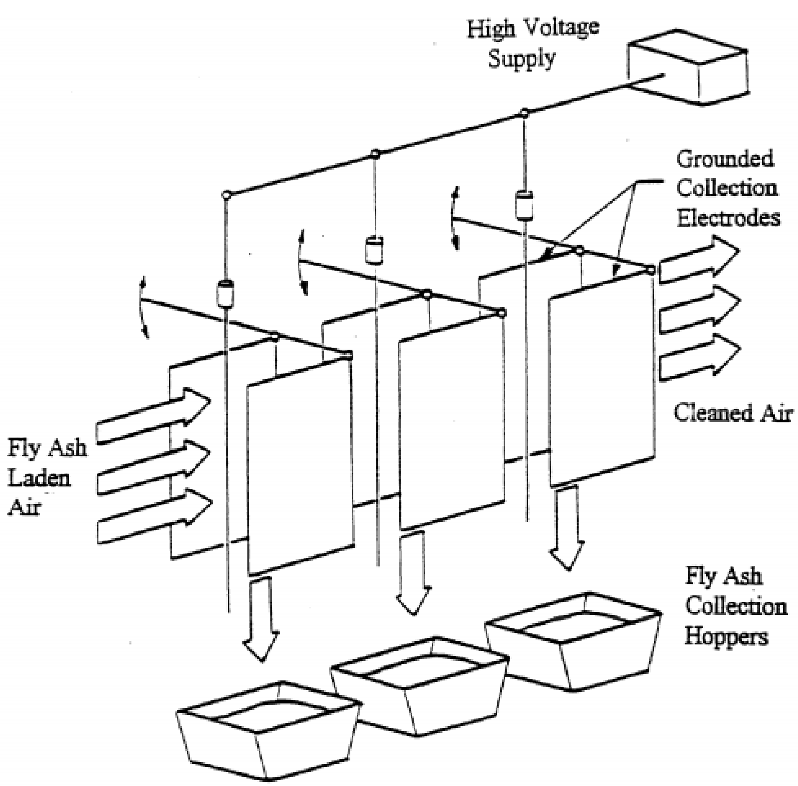


Figure 2. 4: Electrostatic precipitator

(Source ACI 232 Committee report)

Thomas (1999) proposed that the collected fly ash particles segregate in sequential electrostatic precipitator hoppers according to the size and density of the particle. Thus larger/heavier particles tend to accumulate closer to the gas inlet whilst the smaller/lighter particles are collected farther from the inlet. The calcium content of the fly ash is an indicative of how the fly ash will behave in concrete. Lane et al (1982) reported that the shape of fly ash particles is also a function of particle size. The majority of fly ash particles are glassy, solid, or hollow, and spherical in shape as shown below

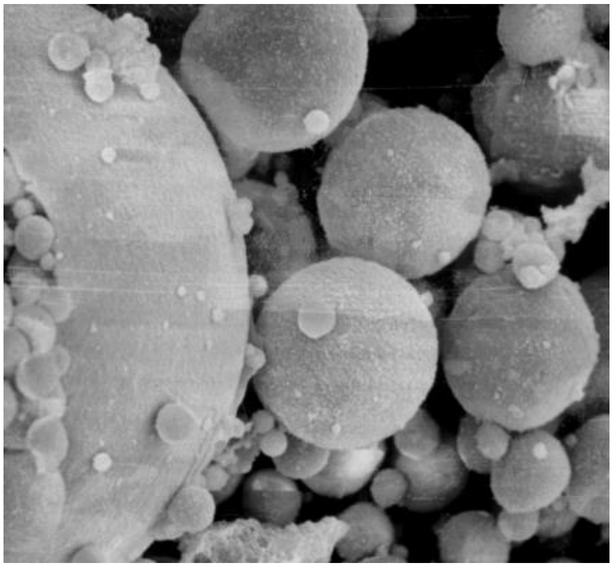


Figure 2. 5: Fly ash showing plerospheres at X 2000 **(Guillot, 2006)**

2.3.1 Physical and chemical characteristics of fly ash

Guillot. (2006) proposed that the effects of fly ash in concrete is attributed to its physical, chemical composition and mineralogical content. Fly ash is mainly classified according to the amounts of the four principal constituents, SiO_2 (35 to 60 percent), Al_2O_3 (10 to 30 percent), Fe_2O_3 (4 to 20 percent), CaO (1 to 35 percent).

Shehata (2000), proposed that the sum of the first three constituents (SiO_2, Al_2O_3, and Fe_2O_3) if greater than 70 percent, the ASTM classifies it as Class F fly ash, whereas when their sum is less than 70 %t, fly ash is classified as Class C.

Table 2. 7: Specifications of Fly Ash based (ASTM C618)

Parameter %	Bituminous	Subbituminous	Northern Lignite	Southern Lignite
SiO_2	45.9	31.3	44.6	52.9
Al_2O_3	24.2	22.5	15.5	17.9
Fe_2O_3	4.7	5.0	7.7	9.0
CaO	3.7	28.0	20.9	9.6
SO_3	0.4	2.3	1.5	0.9
MgO	0.0	4.3	6.1	1.7
Alkalites	0.2	1.6	0.9	0.6
LOL	3	0.3	0.4	0.4
Air Permeability Fineness $m^{2/}kg$	403	393	329	256
45 um Sieve retention	18.2	17.0	21.6	23.8
Density Mg/m^3	2.28	2.70	2.54	2.43

Thomas (1999, proposed that the calcium composition of the fly ash is a parameter, which can be used to determine how the fly ash will behave in the concrete and promote certain characteristics.

Table 2. 8: Specifications of Fly Ash Composition (Thomas 1999)

Group of Fly Ash	Composition of CaO
Type Cl	8-20% CaO
Type F	<8% CaO
Type CH	>20%CaO

The formation of cementitious hydration products due to the reaction with water causes the concrete to harden (Cross et al 2005). The possibility of resultant concrete, which is moderately strong using fly ash as the only cementing material is quite high because of the high calcium content in fly ash. Thomas (1995) highlighted that the reduction in the heat of hydration and expansion control due to the alkali-silica reaction can be predicted by evaluating the mineralogy, and the calcium content of the fly ash. The resistance to sulfate attack is also predictable (Shashiprakash, 2002).

The size and the particulate geometry of a fly ash has a respective influence on its performance properties in concrete. A correlation between the finess and geometrical shape of Class F fly ash with the results of tests by ASTM C 430, 45-mm (No. 325) have been used to establish properties of the concrete (Shashiprakash, 2002).

Lane et al. (1982) proposed that the concrete strength, thawing, abrasion resistance, and resistance to freezing are directly related to the proportion of the fly ash composition, size as well as the source of the fly ash. Lane et al., (1982) concluded that the size within a source of fly ash is a reliable indicator of the performance and properties of the resultant concrete and that increased fineness improves the performance.

Roy et al. (1984) proposed that the density of fly ash ranges from 1.97 to 3.02 mg/m^3 and fine particles often exhibit higher densities however, fly ashes high in iron have relatively higher densities than those high in carbon.

2.3.2 Production and utilization of fly ash in South Africa

The rapid industrialization in South Africa in the 1970s saw an increase in the demand of electricity. Power plants built to meet this demand produces between 3000-3600 MW which indirectly lead to the production of large volumes of fly ash as a byproduct according to R.Kruger et al (2005) . Fly ash is produced by coal-fired electric and steam generating plants. Coal is pulverized and blown into the boilers combustion chamber with air where it ignites generating heat and producing a molten mineral residue. Coarse ash particles, referred to as bottom ash or slag, fall to the bottom of the combustion chamber, whilst the lighter fine ash particles termed fly ash remain suspended in the flue gas.

Fly ash started accumulating in South Africa from the following power stations Matla, Kendal and Lathabo. These power stations are located closer to the coal mines and produce fly ash with good pozzolanic properties. Research into the fly ash started gathering momentum because of the increasing national quantities of fly ash, which at one particular time reached a whooping 20million tones in 2005 (R.Kruger et al, 2005). It was discovered that fly ash could be added to cement in construction and many construction companies developed interest in it and started innovative researches towards fly ash. Fly ash produced from Matla has the following parameters, spherical in shape, low alkali, pozzolanic and a lower carbon content. These parameters lower the water that is required to make concrete, implying that the drying shrinkage will be reduced there by producing smoother concrete. This leads to the production of blended cements with 15 % and 35% fly ash content. Fly ash has been used in construction in the Lesotho Highlands water project in which 40% of fly ash was used in replacement of cement guaranteeing lower temperature raises and reduction in drying shrinkage.

Fly ash is also adopted in the South African polymerization industry in which it is used as fillers. This is because of its spherical shape, which makes it easy to compound and promote easy flow.

Most of the plastic commodities in South Africa contain a special type of fly ash as a filler material.

Fly ash is also being used in Agriculture. The properties of fly ash, which include pH regulation makes it applicable in the fields to regulate the pH levels. It is also being used as a neutralizer (R .Kruger et al, 2005)

R .Kruger et al, (2005) highlighted that the commercialization of fly ash was pioneered in the South African gold mining industry. Gold mines which span as deep as 10 000ft requires supporting structures underneath. These structures were once built from wood, but when fly ash came into light, the support structures were now constructed with fly ash thereby saving deforestation.

2.3.3 Pozzolanic nature of fly ash

Vitruvius, (1960) proposed that fly ash has pozzolanic properties which are almost identical to the naturally occurring pozzolans of volcanic origin. 2000 years ago, the Romans discovered that if volcanic ash with lime, aggregate and water are mixed together, there is production of mortar and concrete. Similarly, if fly ash is mixed with portland cement (which releases CaO during hydration), aggregate and water, it also produces mortar and concrete.

Most of the fly ash contains pozzolanic materials; however, some possess varying degrees of cementitious value without the need for the addition of calcium hydroxide or portland cement. The purpose of a pozzolanic reaction is to convert none cementing silica-rich precursor to a calcium silicate, with good cementing properties.

Pozzolanic reaction in fly ash occurs between calcium hydroxide from the Portland cement, also known as portlandite ($Ca(OH)_2$), and silicic acid chemically symbolized as H_4SiO_4 or as $Si(OH)_4$) as follows

$$Ca\,(OH)_2 + H_4SiO_4 \rightarrow CaH_2SiO_4 \cdot 2\,H_2O \text{ (Calcium silicate hydrate)}$$

This can be abbreviated as $CH + SH \rightarrow C\text{-}S\text{-}H$

The product $CaH_2SiO_4 \cdot 2\ H_2O$ is a calcium silicate hydrate, also abbreviated as C-S-H. This is what constitutes the strong hydration binding in cement.Jennings H. M. (2008) proposed that fly ash contains aluminate, or $Al(OH)_4^-$, which reacts with calcium hydroxide and water to form calcium aluminate hydrates such as C_4AH_{13}, C_3AH_6 or hydrogarnet, or in combination with silica C_2ASH_8. This is a long term irreversible reaction, which involves dissolved silicic acid, water and CaO or Ca $(OH)_2$ or other pozzolans to form a strongly binding cementation matrix. Sufficient amount of free calcium ion and a high pH of 12 and above is needed to initiate and maintain the pozzolanic reaction. This ensures that the solubility of silicon and aluminum ions is high enough to support the pozzolanic reaction (Pellenq et al. 2009)

2.3.4 Effect of fly ash on hydration of cement

Idorn, (1983) indicated that the product of the Class F fly ash reaction is gel-like and denser than Portland cement. It is considered that the fly ash reaction involves the disintegration and dissolution of the spherical glassy structure as a result of attacks by the hydroxide ions supported by the exothermic heat produced during the first hydration stages of the cement (Idorn , 1983). This reaction further consumes the calcium hydroxide resulting in the formation of C-S-H.

Regourd (1983) indicated that a vigorous chemical reaction (hydration) takes place when water is mixed with the spherical glassy fly ash, resulting in the production of aluminum and calcium ions to solution. The amount of exothermic heat produced when fly ash is mixed with cement to make concrete is reduced (Mehta, 1983; Wei, et al., 1984). However, when the quantity of cement used per unit volume of produced concrete is kept at a constant, the introduction of fly ash increased the heat evolved (Mehta, 1983).

Idorn (1984) proposed that, fly ash reaction with cement is such that the initial, and the early curing stages, are such that the first reactions occur with the alkali hydroxides, leading to a reaction with calcium hydroxide, which is the main reaction.

2.3.5 Effect of fly ash on mechanical properties of concrete

Lane, (1983) proposed that the absolute volume in a concrete mixture of cement combined with fly ash is usually above that of cement alone in similar concrete mixtures without fly ash. Fly ash is considered to be of lower density (when the source is carbon concentrated) such that the mass of fly ash used will be equal or slightly greater than the mass of the reduced cement. However, it is dependent on the ratios used for the fly ash and the cement, an increased paste volume results in a concrete with significantly improved performance properties in terms of cohesiveness and plasticity.

Radzinski, (1984) also supported this by highlighting that, increasing the volume of very fine sizes of fly ash can compensate for the reduced volume of aggregate fly ash particle size. The spherical shape of fly ash affects the behavior of the cement paste especially the flow behavior. This usually results in the reduction of the water to cement ratio for a specific workability.

2.3.5.1 Pumpability

It is considered that the use of fly ash results in an improvement in the pumpability of concrete (Rudzinski, 1984). Brown, (1980) proposed that concrete mixtures with lower content of finer sizes or low cement content, have the addition of fly ash making the concrete realize benefits in terms of cohesiveness and resistance to bleeding and segregation. It is also considered that the relative pumpability is increased because of the reduction in friction between the fly ash particles, concrete and the pump line because of the spherical shape of the fly ash particles (Best et al, 1980).

2.3.5.2 Setting time

If cement is replaced partially with fly ash, the setting time of concrete is simultaneously reduced. Jawed et al, (1981) concluded that the Class F fly ashes have a tendency of reducing the early hydration of C_3 S. Grutzeck, et al (1984) realized that the setting characteristics of concrete are influenced by, concrete temperature, type of cement, relative source, fineness and solubility of alkali's in water. Plowman et al, (1984) argued that a proper setting time can be realized if the above-mentioned factors are put into serious consideration.

2.3.6 Fly ash effects on the hardened properties of concrete

2.3.6.1 Temperature rise

It is considered that the reaction between cement and water which significantly generates heat, which significantly influence the development of strength because of the change in the concretes differential volume (Mehta, 1983; Wei, et al., 1984). Most of this heat is considered to be generated during the hydration stages of the cement (Mather, 1974). The following parameters have a direct influence on the heat generated and the rate of hydration on a larger extent. These include placement methodology, temperature during the curing stage, type of cement and its finess just to mention a few (Samarin et al, 1983). Samarin et al, (1983) indicated that the use of fly ash as a cementitious portion in concrete cement can be used to reduce the temperature rise. Reduction of the cement has a direct impact on the heat of hydration in that there will be a correlation between the two parameters.

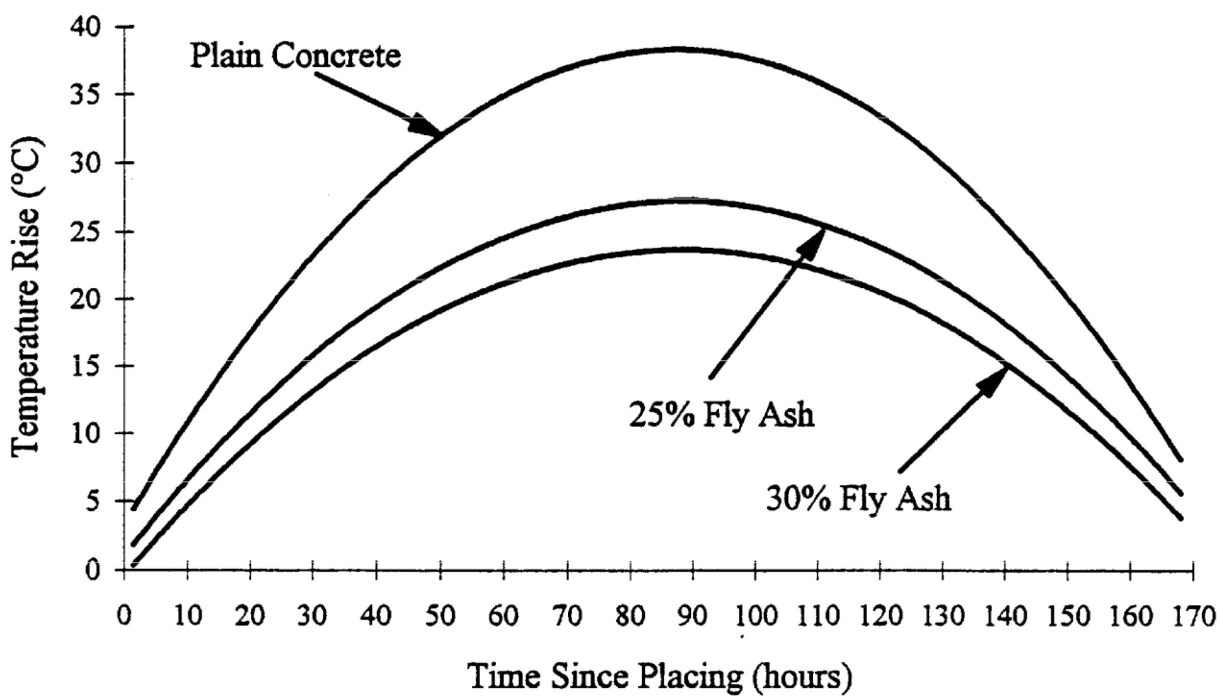


Figure 2. 6: Temperature variation with time (Samarin, Munn, and Ashby, 1983*)*

2.3.6.2 Effect of fly ash on durability of concrete

Experimental researches have shown that concrete having high volume of Class F fly ash exhibited better mechanical and durability properties including a reduced permeability to chloride ions (Atis . 2003) .He highlighted that the presence of Fly ash in concrete reduces drying shrinkage thereby reducing the promulgation of cracks and offering a better resistance to deterioration. Poon et al. (2000) proposed that the replacement of up to 45% class F fly ash, reduced pore diameter and porosity of concrete. Papadakis (1999) observed that there is increased porosity when Class F fly ash replaced cement; however, he noticed a decrease in porosity.

Naik et al. (1994) alluded that when 70% Class C fly ash was added to a cement slurry, there was a reduction in air and water permeability of fly ash concretes at 91 days.

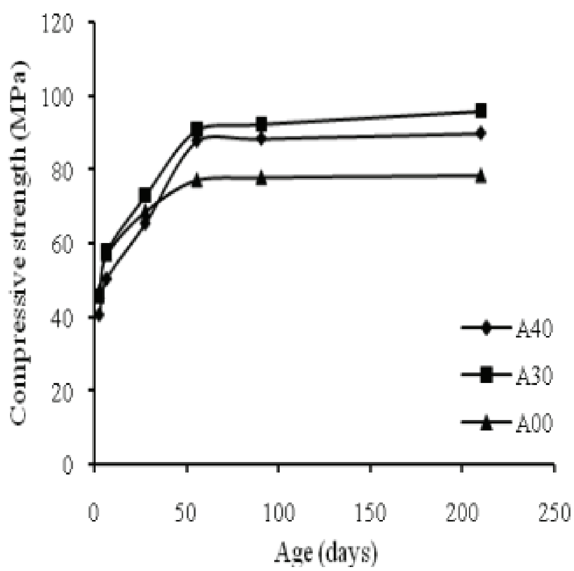


Figure 2. 7: Compressive strength development 0% fly ash,30% fly ash and 40% fly ash (Naith et al 2011)

Figure 2.7 indicate that the addition of fly ash in concrete reduced the compressive strength the earlier age as compared to the sample with no fly ash addition. Concretes with 30% fly ash have shown higher strength gain than those with 40% fly ash. Naith et al. (2011) went on to indicate that the strength of fly ash concretes develops at a higher rate than that of the concrete with no fly ash.

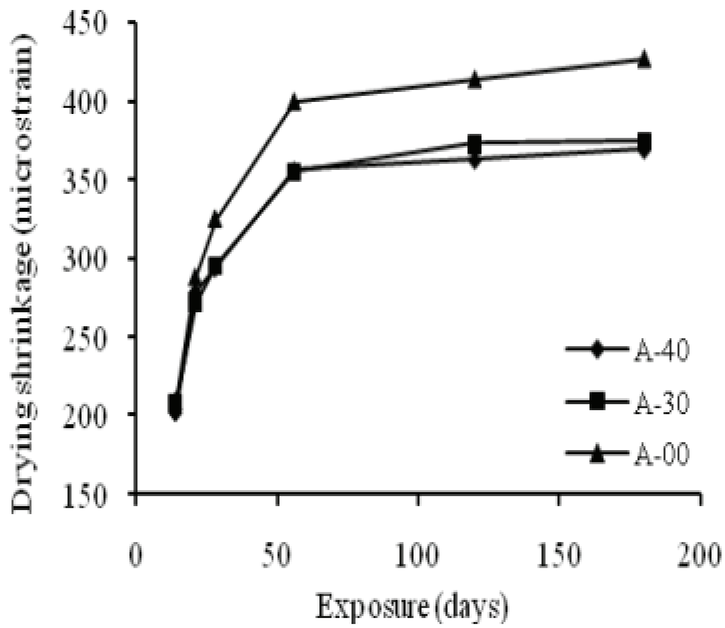


Figure 2. 8: Dry shrinkage development in 0% fly ash, 30% fly ash and 40% fly ash (Naith et al., 2011)

Naith et al, (2011) indicated that the drying shrinkage of 0.0, 30% and 40% fly ash concretes appeared to be similar during the early days of exposure. But concretes with fly addition (A30 and A40) had a reduction in terms of the drying shrinkage compared to concrete with no fly ash. Thus, it is established that application of fly ash in concrete can enhance durability features, according to Naith et al. (2011) but the extent of improvement is dependent on the mix proportions and the properties of the fly ash.

2.3.7 Role of physical and chemical characteristics of fly ash on properties of concrete

The use of fly ash in making concretes has both beneficial and detrimental effects to the performance of the concrete. Addition of fly ash at certain levels optimizes the benefits. However, the negative side has to be considered. The table below provides a summary of how fly ash, when used at moderate to high levels of replacement (15 to 50%), affects the properties of concrete.

Table 2. 9: Effect of Fly Ash on the Properties of Concrete *(Thomas 2007)*

Property	Effect of Fly Ash
Fresh concrete	Improves Workability Reduces water demand Improved pumpability. reduced bleeding
Set time	Extended especially in cold weather. May cause retarded set time
Heat of hydration	Reduced for Class F fly ash Reduced for Class C fly ashes at higher levels of replacement
Early-age strength	Reduced
Long-term strength	Increased.
Permeability and chloride resistance	Reduced
Expansion due to alkali-silica reaction	Reduced.
Sulfate resistance	Increased

2.4 Rheology of oil well cement

It is considered that the rheological properties of cement slurries are dependent on, the temperature variations; there is general trend of increasing the rheological properties with increasing temperature and this is mainly due to the correlation between the formation of hydration products and the surrounding environmental temperature (Saak, 2000, Nelson et al., 2006).

The rheology of cement slurries is dependent on so many factors. These include, the kinetics of cement hydration (Saak, 2000), the composition of the liquid supporting the rheological properties, Nelson et al. (2006) , and the inter particle forces within the rheology of the slurry (Saak, 2000). .Nelson et al. (2006), proposed the solidified volumetric fraction of the cement slurry as one of the factors affecting the rheology of comet.

Guillot, (2006) indicated that the studies on the properties of rheology determines the fluids characteristics; especially the viscosity aspect of the slurry. This parameter is the major determinant of the correlation between the shear rate, also known as the flow rate and the shear stress, which is also a representative of the pressure gradient.

The properties arising because of rheological analysis of cement slurry are a necessary tool for the determination of the properties and characteristics of the output product and are used to give a reliable prediction of the end use and performance of the concrete mixture. The findings of the rheological analysis give an insight of the flow properties of the cement slurry. Of interest is the yield point and plastic viscosity, and frictional behavioral properties that are influenced by the spherical geometry of the ash. These properties can assist in the possibilities of mixing the slurries on the surface and later pump them into the offshore wells.

CHAPTER 3
Experimental Apparatus and Methods

3.1 Particle Size separation

The fly ash particle sizes were separated using the various sieves piled up together as 23µm, 38µm, 45µm, 53µm, 62µm, 75µm and 90um respectively. The sieves were mounted on to the Electronic Sieve Shaker Model ES200 as diagrammatically represented below. The electronic sieve shaker was left to run for a long period, adding the fly ash into the sieve of 90µm on top and collecting a few fly ash at the base collector.

Figure 3. 1: Sieve shaker used to separating the fly ash

3.1.1 The Fly Ash

The raw fly ash sample used in this study was collected from the Secunda (Pty) Ltd in Mpumalanga Province, South Africa. All chemicals and reagents used for experiments and analyses were analytical grade reagents including distilled water.

Figure 3. 2: Fly ash Samples after particle size separation

3.1.2 The Cement

The cement used in this study was obtained from PPC (Pvt) Ltd in South Africa and it was the OPC 55.6 grade cement. It was preferential because the cement does not contain any fly ash.

3.1.3 Chemical Composition

The chemical composition analysis of both the cement and the fly ash was done using the gravimetric analysis method for the Silica and AAS for the other elemental oxide compositions.

3.1.3.1 Compression test Equipment

The Cube press Foote test equipment manufactured by Concrete test equipment was used for the compression strength measurement. The Compressive Strength Test equipment is shown in Figure 3.3.

Figure 3. 3: Compressive Strength Tester

3.1.4 Methodology

Preparation of Fly ash/ Cement Slurry

Cement slurries with a w/c = 0.35 was prepared and hand mixed in a bowl. Distilled water was then be poured into the blender and thoroughly mixed with the cement/fly ash mixture.

Mixing started at a slow speed of 140± 5 rotations per minute for 30 sec and a rubber spatula was used to scrap back any material from the walls of the mixing bowel to the center of the bowel. The mixer was switched to high speed of 285 ± 10 rounds per minute for 40 seconds at ambient room temperature. The slurry was placed in a bowl for 30 minutes at the ambient test temperature to allowing the samples to acquire the same temperature of test whilst rotating the blender at a low speed of 140±5 rpm.

The instruments were set at the test temperature (23degrees Celsius) prior to testing to avoid thermally shocking the samples. Whilst the total time incurred between the starting of the mixing of the cement slurry and the initial rheological test was made constant to avoid variable results because of exogenous effect (Williams et al., 1999; Chow et al., 1988; Roy and Asaga, 1979).

3.1.5: Rheometric Tests

The viscosity, shear rate and shear stress of the samples were analyzed using a rheometer known as Rheolab CC Anton Paar Model with a temperature-regulating device. The tests were run at ambient temperature because the rheometer has a disadvantage of having very low temperature limits. This made it a bit difficult to mimic the temperatures and the pressures in the oil well

Figure 3. 4: Anton paar Rheometer CC

The following methodology was used for the rheometer tests for the fly ash/cement slurry different composition and particle size mixtures.

The slurry sample was poured into the coaxial cylinder of appropriate size and fixed on to the rheometer at ambient temperature and the sample was tested for viscosity measurements at variable shear rates and shear stress at continuous rotation. The slurry sample was not exposed to a descending shear rate to obtain a curve showing a downward flow curve.

3.1.6 Compressive Strengths

The following steps were followed for the compressive strength test

A paste of 0.35 w/c containing both cement and fly ash of the different particle sizes was prepared and mixed with distilled water. Slurry were scooped into a mould, containing different ash compositions and particle sizes leading to the storage of the specimens at room temperature for 48 hours in the mould;

The samples were removed from the mould after 48 hrs and wet cured in lime-saturated water resembling the pH of ocean water for some time and later on cured in air at ambient temperature. The molds were cut into 50mm specimens and were tested by slowly bringing the compression blocks to bear on the samples without shock until failure occurs and the compressive strength was calculated as followed

$$\textbf{Compression Strength (MPa)} = \frac{\textbf{Load in N}}{\textbf{Area in mm}^{\mathbf{2}}} \tag{3.1}$$

Table 3.1 below shows the particle size and the corresponding number of days that the curing mold was stored for. Smaller particles sizes were stored for relatively longer days whilst larger particles sizes where stored for reasonably fewer days.

Table 3. 1: Periods of curing molds

Particle Size μm	Days of storage
25	39
38	27
45	25
53	21
63	18
75	17
90	16

3.1.7 Rate of Water Loss

The rate of water loss of the cement slurry was measured by preparing 0.35w/c cement fly ash slurry for the different particle sizes and different cement to fly ash compositions. The following steps were followed:

Cement/fly ash slurry with the following fly ash compositions was prepared 2.5%, 5%, 7.5%, 10%, 15%, 20%, 30% and 40% for the 25um, 38um, 45um, 53um, 68um, 75um and 90um particle sizes respectively.100 ±5g of the prepared slurry was put in an evaporating dish for each of the fly ash compositions and the slurry's initial weight was measured and recorded. The slurry's weight was recorded daily for 16 days and calculation of the rate of weight loss for the slurry was done as follows

$$\textbf{Water } \boldsymbol{Loss} = \frac{(\textbf{initial weight} - \textbf{ weight at 16days}}{\textbf{16days} * \textbf{24hrs}} \qquad (3.2)$$

CHAPTER 4

Results and Discussions

4.1 Chemical Composition of Cement and Fly Ash

The chemical composition of the characterized cement and fly ash is given in the Table 4.1

Table 4. 1: Chemical composition of the characterized fly ash and cement

SAMPLE	% CaO	% FeO	% SiO2	% Al2O3	% MgO	% Na2O	% K2O
Cement	8.72	3.78	48.13	21.05	5.04	0.82	0.69
Fly Ash	42.28	0.61	35.66	11.49	6.23	0.58	0.61

Thomas (1999) classified the investigated fly ash sourced at SASOL Secunda as type CH with a CaO content of 42.28% (above 20 %) as seen in Table 4.1. According to the ASTM C618, the sum of SiO_2, Al_2O_3 and FeO is 47.76 % (less than 70 %), the investigated fly ash is classified as Class C. Class C fly ash has self-cementing properties, with tendency to harden over time.

4.2 Compression Tests

The compression tests were carried out using a hydraulic cube pressure tester and results are shown in Figure 4.1 and Table 4.2 below. The table shows the Fly ash composition, particle size and the corresponding compression strength. Figure 4.1 will indicate a plot of the same to establish a trend and a relationship if it exists between the fly ash composition, compression strength and the particle size.

Table 4. 2: Compression strength (MPa) for different particle sizes for different cement to fly ash proportions

Fly Ash Composition %	25um	38um	45um	53um	63um	75um	90um
40	2.6	2.2	3.2	1.6	4.4	4	2
30	2.8	4.6	3	3.4	9	6.6	5
20	6.2	5.8	2.2	3.6	5	10.6	4
15	8.8	9.4	2.6	2.6	6.8	5.2	2.4
10	3.8	12.2	7.4	4	7.8	1.2	4
7.5	2.4	4	7.2	2.6	9	5.2	3.4
5	6.2	4	5.6	3	5.6	10.6	5.2
2.5	2.8	7.8	5	4.6	10.8	6.2	10

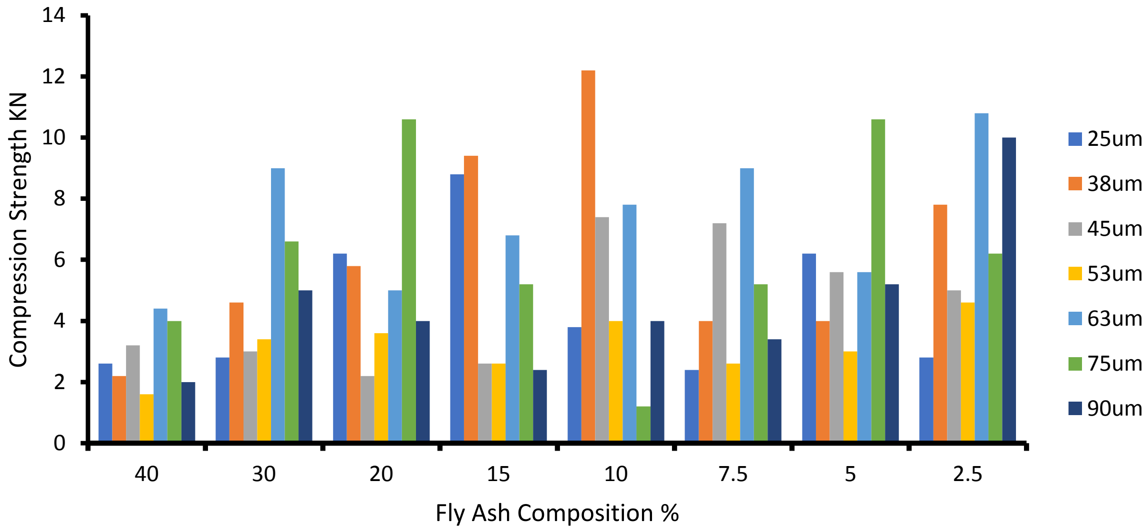


Figure 4. 1: Compression strength (MPa) different particle sizes for different cement to fly ash proportions

Figure 4. 1 showed that addition of 10% fly ash provide higher compression strength at 38um particle size of the fly ash, whilst particle size of 75um recorded the least compression strength for the same fly ash content (10% fly ash). Higher fly ash content (40%) regardless of particle size showed very low compression strength with a maximum of 4.4MPa at 63um particle size. This shows that a higher proportion of fly ash reduces the compression strength because there will be a significant reduction in the hardening of the slurry due to a reduced level of hydrating substances found in the cement particularly the C-S-H bonds.

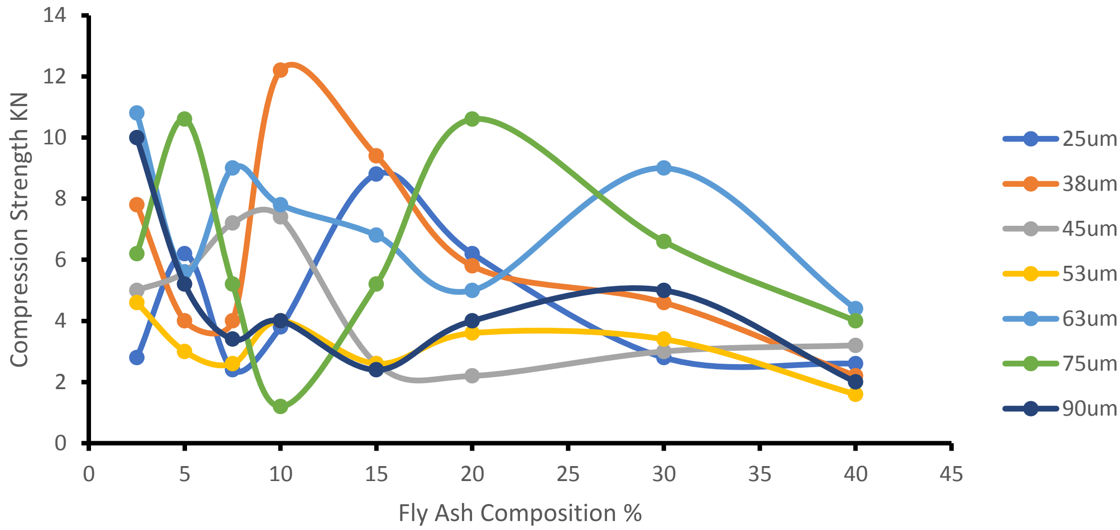


Figure 4. 2: Compression Strength (MPa) behavior of different particle sizes with various fly ash content

Figure 4.2 showed a damping behavior of compression strength for cement – fly ash at various sizes and fly ash content. As fly ash content increase, the amplitude decrease. Figure 4.2 clearly indicates the highest achieved compressive strength at 10% fly ash and the lowest at the same fly ash content but for a much higher particle size 75um of fly ash. Larger particle sizes reduce the strength of the resulting concrete because of the presence of numerous gaps as the particles settle, which create space for movement when the concrete material is under stress.

At higher fly ash composition of 40%, the compressive strength for the range of the particle sizes is generally lower .This is compared to the compressive strength at 2.5% fly ash, which is quite high for most of the particle sizes. This shows that general substitution of cement with fly ash reduces the interactive forces of attraction (C-S-H) between the molecules.

Particle size 38um recorded the highest compressive strength whilst the lowest was recorded at 75um. This low compositions of fly ash and smaller particle sized molecules has a general tendency of increasing the compressive strength

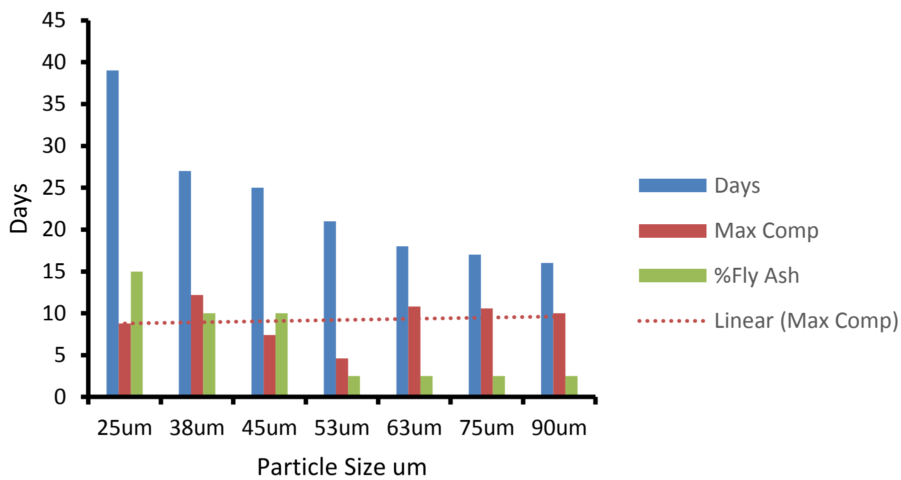


Figure 4. 3: Maximum Compression Strength per particle Size per Days cured

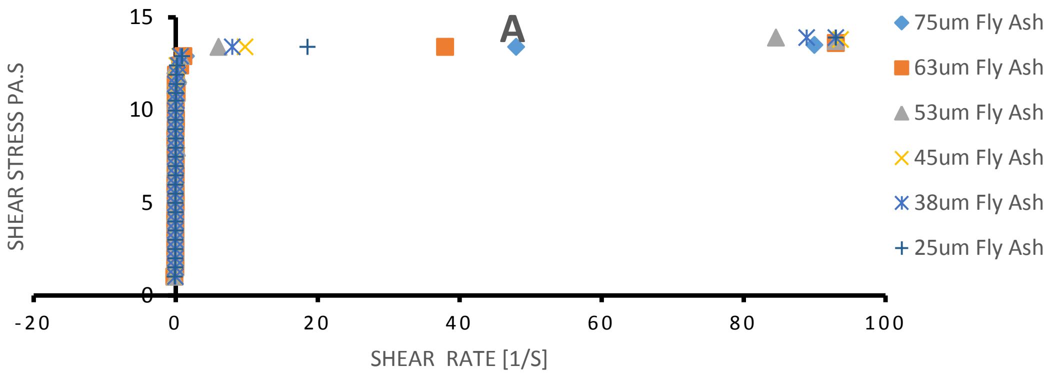
4.3 Rheology Tests

All investigated fly ash/cement slurries exhibited non-Newtonian and shear thinning behavior by having the viscosity decreasing with increasing shear rate. Shear thinning is described as the non –Newtonian behavior in which fluids viscosity decreases with increasing shear strain (Guillot, 2006). This is usually as excluding time dependent effects such as thixotrophy. Because the recovery of a liquid to its initial state always requires a none-zero time, shear thinning thus becomes a special case of thixotropic behavior. Instead of gradually flocculating, the microstructures of the liquid returns to normal as soon as the shear is removed. Whereas a liquid or a suspension exhibits thixotropic behavior when the viscosity at all the shear rates is decreased for some duration after agitation.

The fly ash/cement slurries also followed the Bingham plastic mode as they required minimum stress before they started flowing. This was attributed to non-Newtonian fluids but as soon as they started flowing, they started behaving as Newtonian fluids.

4.3.1 Shear Rate vs Shear Stress

The curve data was fitted on a linear equation using ordinary least squares regression to determine a slope (plastic viscosity) and an intercept (yield stress) according to the Bingham model



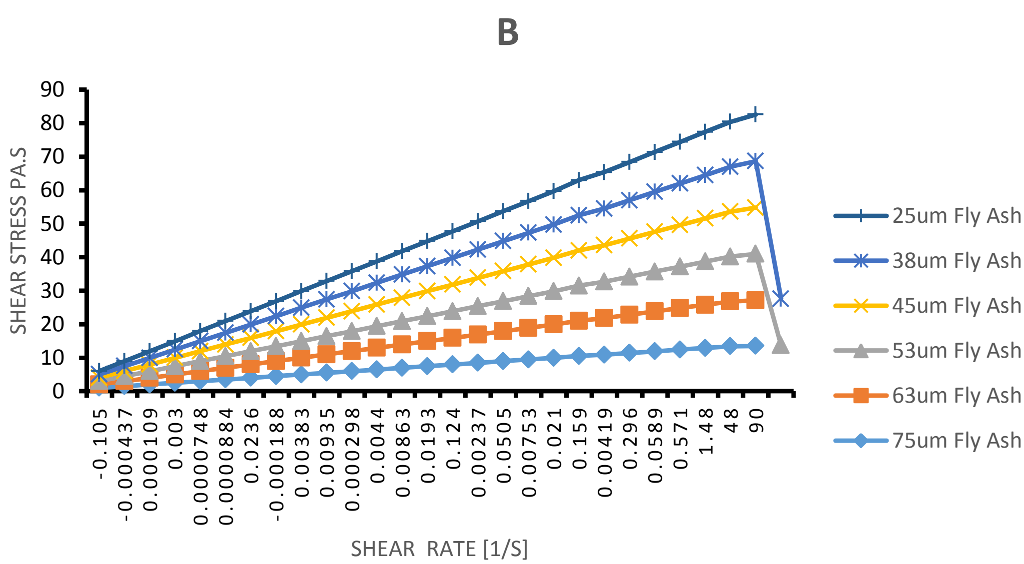
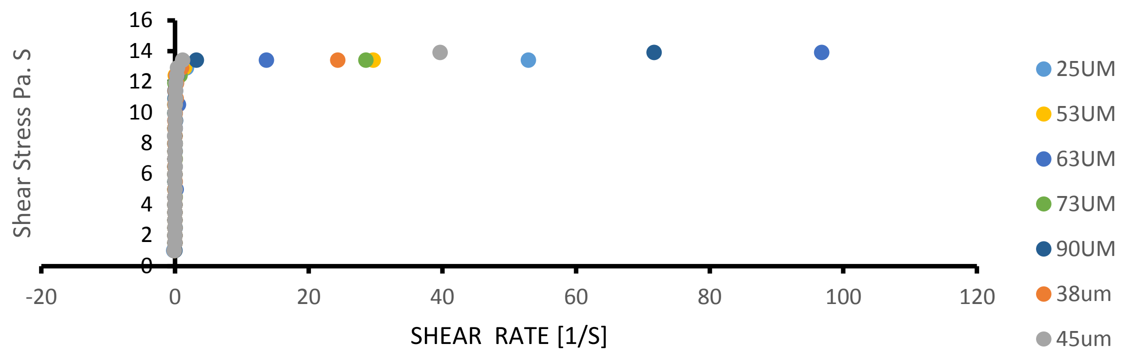
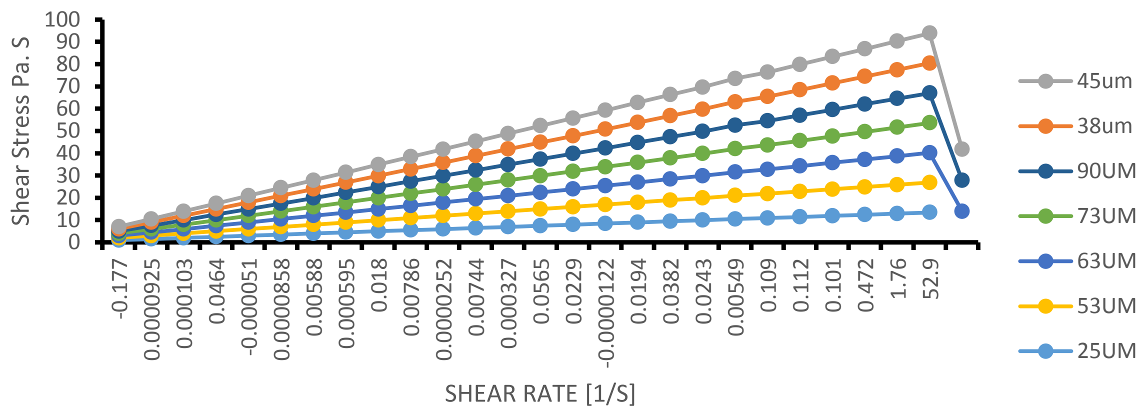


Figure 4. 4: Share stress behavior of 15 % Fly ash content

Figure 4. 4 (B) shows that the particle size 25um has exhibited the highest shear stress level whilst 75um particle size exhibiting the least. This shows that increasing the particle size of fly ash in the cement slurry, decrease its shear stress.



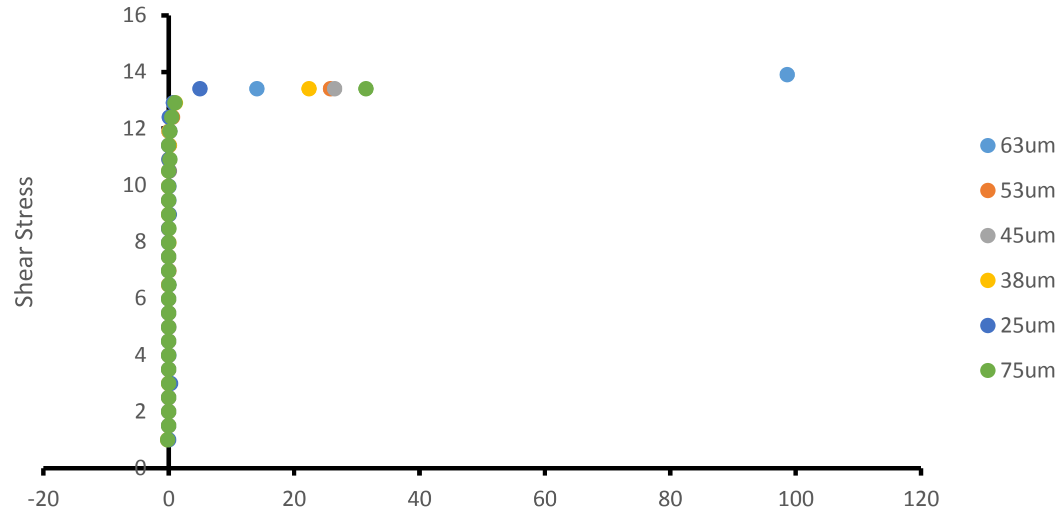
a)



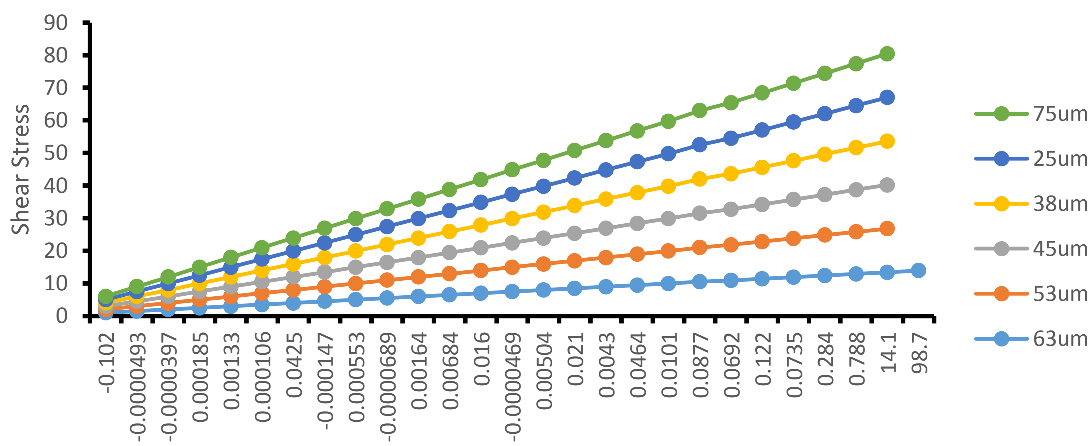
b)

Figure 4. 5: Shear stress behavior against shear rate for 35 % Fly Ash

Figure 4. 5 .b) shows that the particle size 45um has exhibited the highest shear stress level on the line graphs with the 25um particle size exhibiting the least. Increasing the content of fly ash in the cement slurry decrease the shear stress of small particle size, and increase the shear stress of higher particle size. The results observed in Figures 4.4 and 4.5 show that the compressive strength is inversely proportional to the fly ash particle size for low ash content, and proportional to the fly ash particle size for High ash content. Same behavior was observed for 65 % fly ash as seen in Figure 4.6.



a)



b)

Figure 4. 6: Shear stress behavior for 65 % fly ash content

4.3.2 Apparent Viscosity

A high viscosity liquid requires more power to pump than a low viscosity one hence the determination of the apparent viscosity at a specific shear rate will enable one to determine which particle size, thus composition exhibits a favorable apparent viscosity making it easier to pump the cement slurries into oil wells. Knowing its rheological behavior, therefore, is useful when designing pumping and piping systems. The apparent viscosity η_a is reported as the ratio between the measured shear stress to the applied shear rate (ŗ/ŷ) at a specific shear rate. Apparent viscosity may be defined mathematically by this formula:

$$Apparent\ viscocity(\eta a) = \frac{Shear\ stress(ŗ)}{Shear\ rate(\hat{y})} \tag{4.1}$$

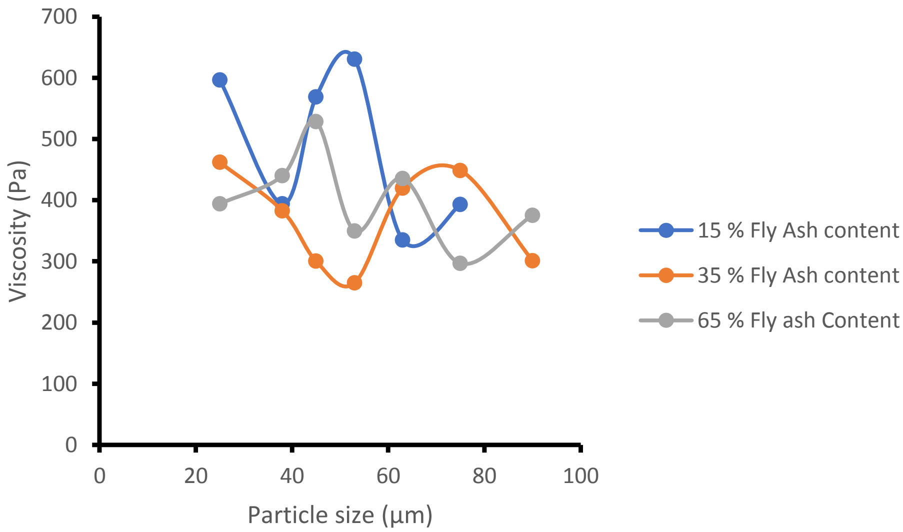


Figure 4. 7: Viscosity behavior against fly ash particle size at various fly ash content

Figure 4.7 shows a wave behavior of viscosity as function of particle size. It can be seen that low fly ash content (15 % fly ash) had higher viscosity amplitude. There is a generally higher apparent viscosity at 25um both for the 15% and 35% fly ash substitution of approximately 596.59 and 461.86 Pa respectively, whilst the apparent viscosity at 65% fly ash substitution is generally low at 394.17Pa. This is due to the increase for fly ash, which according to the chemical composition has a lower Silica of 35.66% content that is involved in the flocculation or solidification. In comparison to the cement Silica content of 48.13%, which is quite higher.

The particle size 25um generally has a higher apparent viscosity because the finer particles are able to compact all the spaces in the matrix and forming stronger interparticle forces.

This makes the adherence forces between the parallel plates much stronger resulting in a higher viscosity, which can be generalized as a measure of resistance to flow.

4.3.3 Yield Stress

Two mixtures may behave similarly at an applied shear rate, but the yield stress may be completely different such that the measurement of a concretes yield stress and plastic viscosity is essential to establish the flow behavior of a concrete paste. Table 4.3 displayed yield stress for various particle size.

Table 4. 3: Yield stress of various particle sizes at different fly ash content

Particle Size	15% Fly Ash 85%Cement	35%Fly ash 65%cement	65%Fly ash 35% Cement
75um	1	0.9	0.8
63um	1	0.9	0.8
53um	1	1	0.8
45um	1	1	0.8
38um	1	0.9	0.8
25um	1	1	0.9

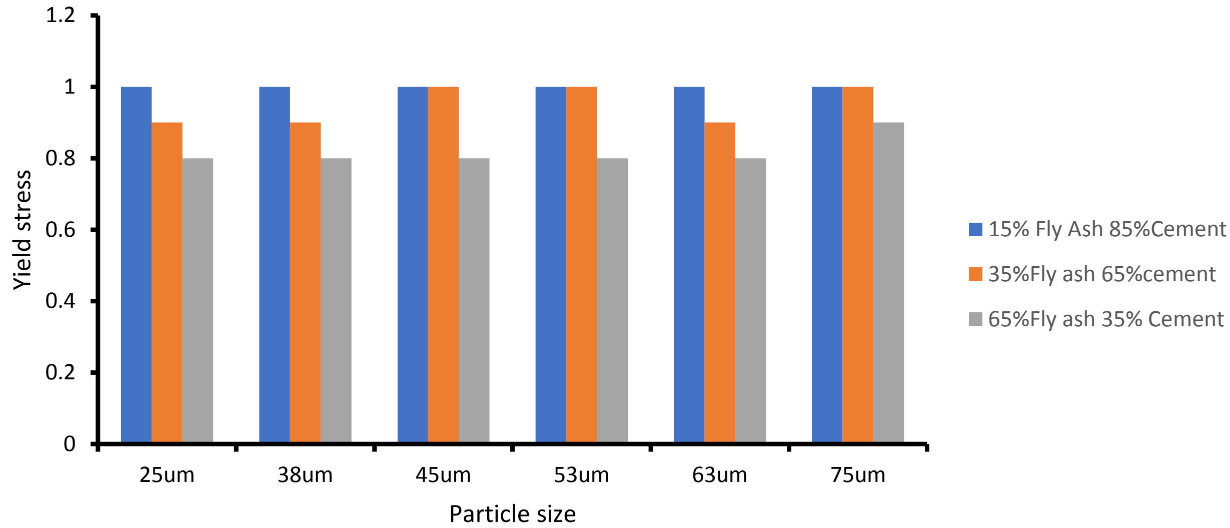


Figure 4. 8: Yield stress behavior at various particle size

Figure 4.8 indicates that the 35% fly ash and 65% fly ash content exhibited much lower yield stress compared to the 15% fly ash, which showed higher yield stress. This shows that there is a general trend in the reduction of the yield stress with increasing fly ash content. Malhotra (1996) highlights that the replacement of cement with fly ash decreases the yield stress, as there is a proportional decrease in the particle density of the cement. This will intern reduces the number of the flocculated cement particle.

It is quite difficult to quantify the differences in yield stress as result of the differences in particle sizes. However, there is a much clearer indication that 75um, 63um and 38 um particle sizes have a generally lower yields stress with respect to 35% fly ash composition. Larger particle sizes have a tendency of locking such that the ease of particles sliding over each other is reduced as compaared to smaller particle sizes. Bentz, etal.(2012) postulates that Yield stress is dominated by the particle density of the cement component, with the fly ash mainly acting as a diluent that effectively decreases the cement particle number density.

4.3.4 Water Loss

As discussed above, water retention is an important parameter for cement slurry to be able to maintain its pumpability.

Table 4. 4: Water retention data behavior against fly ash particle size and amount

Fly Ash Particle size	2.5%	5%	7.50%	10%	15%	20%	30%	40%
25um	0.0482	0.055	0.0522	0.0531	0.0468	0.0524	0.0541	0.0504
38um	0.0494	0.0497	0.0501	0.0482	0.0454	0.0489	0.048	0.0539
45um	0.0434	0.0444	0.0424	0.0445	0.0428	0.0452	0.0466	0.0447
53um	0.0489	0.0505	0.0511	0.0513	0.0512	0.0484	0.047	0.0479
63um	0.0407	0.0427	0.04	0.0402	0.0414	0.0427	0.0399	0.0409
75um	0.0439	0.0442	0.0447	0.0439	0.0438	0.0488	0.0449	0.0458
90um	0.0477	0.0502	0.05	0.0516	0.0498	0.0503	0.0505	0.0497

The capability of slurry to be able to retain water is of vital in determining the slurries behavioral properties. This will enable the slurry to be mixed onshore and then transported offshore for casing

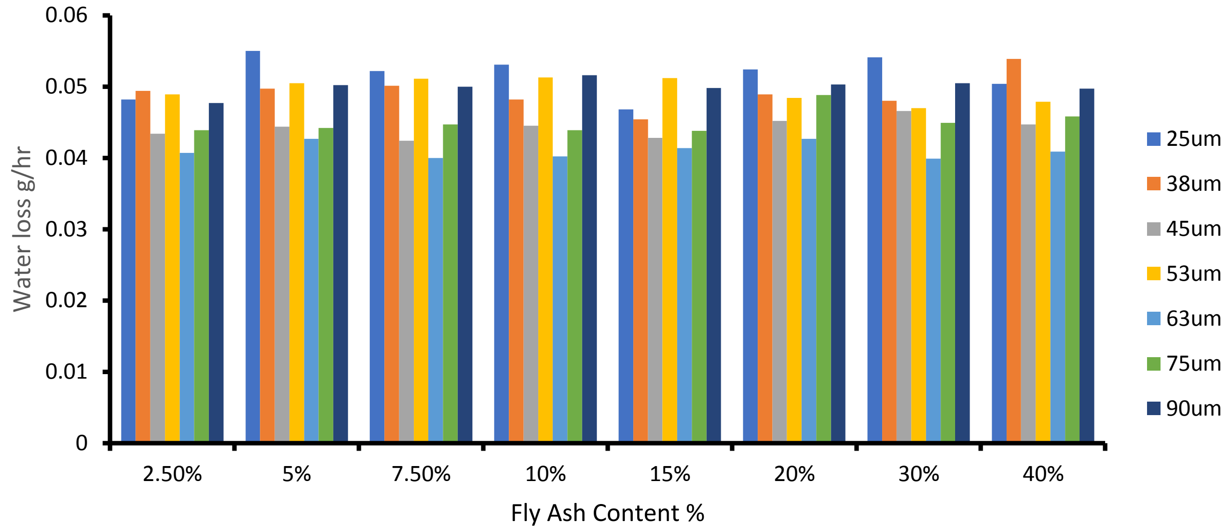


Figure 4. 9: Water loss behavior for various fly ash content and particle size

Figure 4.9 showed a non-uniform trend of water loss for various fly ash content and particle size. The lowest particle size (25um) had shown to loss more water for different fly ash content in general (5%, 7.5%, 10%, 20% and 30%). The highest water loss being recorded at 5% fly ash content. Smaller particle sizes tend to be more attracted to each other due to the inter particle forces existing between the particles. This makes the inter particle space reduced such that the water molecules are pressed out of the space exposing them to higher rates of evaporation leading to a higher water loss. Larger particles create lower forces of attraction due to the larger inter particle spaces thereby creating room for the water molecules to settle within the space. This shields the water molecules from exposure to higher rates of evaporation and thus retaining the water molecules.

4.3.5 Graphical Trend Analysis

Figure 4.1 on compression tests shows that a higher proportion of fly ash reduces the compression strength because of the significant reduction in the hardening of the slurry due to a reduced levels of hydrating substances found in the cement particularly the C-S-H bonds. Whereas lower proportions of fly ash increased the compression strength of the cement-to-fly ash composition. The results observed in Figures 4.4 and 4.5 show that the compressive strength is inversely proportional to the fly ash particle size for low ash content, and directly proportional to the fly ash particle size for High ash content. Figure 4.7

Shows that the particle size 25um generally has a higher apparent viscosity because the finer particles are able to compact all the spaces in the matrix thereby forming stronger interparticle forces which results in a higher resistance to flow. Figure 4.8 shows that there is a general reduction of the yield stress with increasing fly ash content. This is because the replacement of cement with fly ash results in a proportional decrease in the particle density of the cement. This will intern reduces the number of the flocculated cement particle thereby reducing the formation of (C-S-H) bonds making it easier for the interparticle forces to break during stress. Figure 4.9 showed a non-uniform trend of water loss for various fly ash content and particle size. However, smaller particle sizes tend to be more attracted to each other due to the forces existing between the particles making the inter particle space reduced leading to the water molecules being pressed out of the space exposing them to higher rates of evaporation. Larger particles create lower forces of attraction due to the larger inter particle spaces thereby creating room for the water molecules to settle within the space.

CHAPTER 5

Conclusion and Recommendation

1.0 Conclusion

The research revealed that addition of fly ash to 65% composition slightly reduced the yield stress. This implies that when pumping oil well cement, which are substituted with fly ash, there is a reduction in the force required to pump the cement slurry. Finely ground cement/fly ash particle size also has a tendency of reducing the yield stress making it is easier to pump oil well cement slurry to the offshore oil wells.

Compression tests indicated that 10% fly ash has a higher compression strength at 38um particle size. However, 40% of fly ash added at the different particle size indicated very low compression strength compared to other compositions. Therefore, there is a relationship between addition of fly ash and compression strength. Higher proportions of fly ash tend to reduce the resultant compression strength.

The 25um particle size recorded the highest rate of water loss at the following fly ash/cement substitution compositions, 5%, 7.5%, 10%, 20% and 30%.The highest rate of water loss being recorded at 5% fly ash composition. The research therefore indicates that larger particle sizes can reduce water loss thus keeping the cement/fly ash slurry wet enough to be pumped to the offshore wells for casing.

1.1 Recommendations

The research proved that there is a higher apparent viscosity at 25um for both 15% and 35% fly ash substitution. This shows that larger particle sizes have a lower viscosity. The substitution of cement with 65% fly ash reduced the yield stress during the pumping of the slurry to the offshore leading to a reduction in electricity usage. According to the Portland cement Association (PCA) labor and energy survey, the average consumption of electricity is equal to 76.73KW h per ton of cement. If 65% of fly ash is substituted to the cement, the reduction of electricity is equal to

Electricity reduction = 0.65 x 76.73= 49.8745 KWh/ton of cement

This indicates that use of fly ash as supplementary cementitious material has a realistic benefit towards the reduction of pollution from cement producing companies as well as saving electricity. Thus, a recommendation for further studies is given to carry out the actual simulation of the high pressures and high temperatures to which the cement/fly ash slurries will be exposed to. This will enable the research to describe exactly how the slurries will behave. Furthermore, studies have to be carried out using correct instruments and equipment for the separation of the fly ash particle sizes so that the research can distinguish precisely the best performing particle size.

Concerning rheological tests, the recommendation is on the use of a rheometer with both higher temperatures and pressure variables that help to simulate the behavior of the slurries during pumping the slurry into the oil well casing. The study did not included sand in the preparation of cement/fly ash slurry; recommendation is made to incorporate sand of the same average size as the fly ash to increase the compression strength of the specimen blocks.

Lastly, more research must also be done on the hardened concrete after setting in the casing under exposure to the same high temperature and pressure.

References

1. Al-Martini, S., 2009. *Investigation on rheology of cement paste and concrete at high temperature. PhD Thesis, the University of Western Ontario* (Vol. 70, No. 08).
2. Bossis, G. and Brady, J.F., 1989. The rheology of Brownian suspensions. *The Journal of chemical physics*, *91*(3), pp.1866-1874.
3. Chow, T.W., McIntire, L.V., Kunze, K.R. and Cooke, C.E., 1988. The rheological properties of cement slurries: Effects of vibration, hydration conditions, and additives. *SPE Production Engineering*, *3*(04), pp.543-550.
4. Domone, P.L. and Thurairatnam, H., 1988. The effect of water/cement ratio, plasticizers and temperature on the rheology of cement grouts. *Advances in Cement Research*, *1*(4), pp.195-206.
5. Guillot, D., 1990. 4 Rheology of well cement slurries. In *Developments in Petroleum Science* (Vol. 28, pp. 4-1). Elsevier.
6. Nehdi, M., Mindess, S. and Aïtcin, P.C., 1998. Rheology of high-performance concrete: effect of ultrafine particles. *Cement and Concrete Research*, *28*(5), pp.687-697.
7. Nelson, E.B., Michaux, M. and Drochon, B., 2006. Chemistry and characterization of Portland cement. *Well cementing*, *2*.
8. Park, C.K., Noh, M.H. and Park, T.H., 2005. Rheological properties of cementitious materials containing mineral admixtures. *Cement and concrete research*, *35*(5), pp.842-849.
9. Sybertz, F. and Reick, P., 2014, April. 2 Effect of fly ash on the rheological properties of cement paste. In *Rheology of Fresh Cement and Concrete: Proceedings of an International Conference, Liverpool, 1990*(p. 13). CRC Press.
10. ASTM C 311-00: Standard test methods for sampling and testing fly ash or natural pozzolans for use as a mineral admixtures in Portland-cement concrete, Annual Book of ASTM Standards, Philadelphia
11. Cook, J.E., 1983. Fly ash in concrete-Technical considerations. *Concrete International*, *5*(9), pp.51-59.
12. Davis, R.E., 1954. Pozzolanic materials-with special reference to their use in concrete pipe. *American Concrete Pipe Association, Technical Memo*.

13. Dunstan, E., 1984. *Fly Ash and Fly Ash Concrete, Bureau of Reclamation Rept* (pp. 20-30). ERC-82-1, May.
14. Gebler, S.H. and Klieger, P., 1986. Effect of fly ash on physical properties of concrete. *Special Publication*, *91*, pp.1-50.
15. Tikalsky, P.J., Huffman, M.V., Butler, W.B., Jensen, J.S., Popovics, S., Call, B.M., Keck, R., Prusinski, J., Carrasquillo, R.L., Kosmatka, S.H. and Reddy, D.V., 1996. Use of fly ash in concrete. *ACI Committee*, *232*.
16. Lane, R.O., 1983. Effects of fly ash on freshly mixed concrete. *Concrete international*, *5*(10), pp.50-52.
17. Best, J.F., 1982. Properties and use of fly ash in Portland cement concrete. *Concrete International*, *4*(7), pp.81-92.
18. Lovewell, C.E. and Washa, G.W., 1958, June. Proportioning concrete mixtures using fly ash. In *Journal Proceedings* (Vol. 54, No. 6, pp. 1093-1101).
19. Luke, W.I., 1961. *Nature and distribution of particles of various sizes in fly ash* (No. AEWES-TR-6-583). Army engineer waterways experiment station vicksburg miss.
20. Minnick, L.J., Webster, W.C. and Purdy, E.J., 1971. Predictions of the effect of fly ash in Portland cement mortar and concrete. *Journal of Materials*.
21. Jennings, H.M., 2008. Refinements to colloid model of CSH in cement: CM-II. *Cement and Concrete Research*, *38*(3), pp.275-289.
22. Pellenq, R.J.M., Kushima, A., Shahsavari, R., Van Vliet, K.J., Buehler, M.J., Yip, S. and Ulm, F.J., 2009. A realistic molecular model of cement hydrates. *Proceedings of the National Academy of Sciences*, *106*(38), pp.16102-16107.
23. Saha, A.K. and Sarker, P.K., 2017. Sustainable use of ferronickel slag fine aggregate and fly ash in structural concrete: mechanical properties and leaching study. *Journal of Cleaner Production*, *162*, pp.438-448.
24. Chindaprasirt, P., Jaturapitakkul, C. and Sinsiri, T., 2005. Effect of fly ash fineness on compressive strength and pore size of blended cement paste. *Cement and Concrete Composites*, *27*(4), pp.425-428.
25. ASTM, C., 2012. Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete. *C618-12a*.

26. ASTM, C., 1998. Standard specification for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in concrete. *1998 Annual Book of ASTM Standards*, *4,* pp.pp-293.