THE USE OF SOUTH AFRICAN COAL FLY ASH (CFA) AS AN ADDITIVE TO OIL WELL CEMENT DURING CEMENTING OPERATION

By

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A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in partial fulfilment of the requirements for the degree of Master of Science in Engineering

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11 August 2015

DECLARATION

I declare that this research report is my own unaided work. It is being submitted to 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.

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(Signature of Candidate)

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ABSTRACT

This work reports for the first time in open literature, the beneficiation of South African coal fly ash (CFA) in oil well cementing operation. Firstly, CFA was characterized using X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), proximate and particle size analyses. Silica (SiO_2) was then extracted from the CFA through acid leaching using 3M hydrochloric acid (HCl) at 100 ^oC for 6 hours. The extracted SiO_2 was filtered out, purified through successive demineralized water washings and dried in an oven at 200 ^oC for 2 hours. The physicochemical properties of the extracted SiO_2 were analyzed using XRD, SEM and Fourier Transform Infrared spectroscopy (FTIR).

Furthermore, the extracted SiO_2 was reacted with sodium hydroxide (NaOH) at 80 ^oC and atmospheric pressure to produce sodium silicate, commonly used oil well cement (OWC) slurry extender. The physicochemical properties of the synthesized sodium silicate (CFA-Na_2SiO_3) were compared to those of a commercial sodium metasilicate (com-Na_2SiO_3) using SEM, XRD and FTIR analyses.

Moreover, OWC slurries with varying compositions of cement, distilled water and 2 % $CaCl_2$ by-weight-of-water (BWOW) were prepared and extended using the synthesized CFA-Na_2SiO_3 and com-Na_2SiO_3 at compositions ranging from 0.25 – 2.5 % by-weight-of-cement (BWOC). A comparative study to evaluate the densities, compressive strength, and

rheological properties of the slurries was carried out in accordance with the specification for materials and testing for Well Cements (API, 1990).

The results obtained showed that the South African CFA belongs to Class F and contains 58 % SiO_2, which is the desired component in this study. The physicochemical properties of the extracted SiO_2 indicate that it is amorphous in nature. In addition, the synthesis protocol for making CFA-Na_2SiO_3 using the extracted SiO_2 and NaOH, which was at a mild temperature compared to the traditional energy-intensive method, indicate the possibility of energy saving of the method used. Moreover, the physic-chemical properties of the synthesized CFA-Na_2SiO_3 are consistent with that of com-Na_2SiO_3, indicating the purity of the as-prepared CFA-Na_2SiO_3.

Results obtained from the comparative study between the OWC slurries indicate that the slurries extended with CFA-Na_2SiO_3 have slightly lower densities, lower viscosities and higher compressive strength compared to those extended with com-Na_2SiO_3. This indicates that CFA-Na_2SiO_3 slurries would be easier to pump and preferable where early strength development is critical. Analysis of the thickening times of the slurries could not be done at the time when this study was carried out because the HPHT consistometer at the Baker Hughes South Africa was faulty, and at the time this report was submitted it has not been repaired. Since this study forms a part of a taught MSc degree programme in Petroleum

Engineering (otherwise known as 50:50), the time allotted for research was too little for a comprehensive research. Consequently, thickening time analysis of the slurries could not be conducted. However, results from this study could be a platform upon which further research development in this area could be built. Hence, it is recommended that future studies should consider the analysis of thickening time of the slurries.

This report thus opens up a way for the beneficiation of South African coal fly ash in the petroleum, oil and gas industry. Evaluation of the performance of the CFA-Na_2SiO_3 in remedial cementing as a complement to a cement squeeze and for blocking gas migration is recommended for future studies. Furthermore, the evaluation of the performance of the CFA-Na_2SiO_3 as an additive to drilling fluid is also recommended.

DEDICATION

I dedicate this work to my mother, Elizabeth Chirunga who has always been supportive, and to my husband, Andrew Kaduku who makes my life beautiful and each day worth looking forward to.

ACKNOWLEDGEMENTS

First and foremost I would like to praise the Almighty God for giving me the strength, focus and will in my academic endeavors. Secondly, I would like to extend my heart-felt gratitude to all the people who provided the much-needed assistance to make this project successful. It is in this light that special thanks go to the following:

- ✓ My research supervisor Dr M. O. Daramola, for his constant support throughout the synthesis of this project. His guidance and patience helped me to develop academically tremendously.
- ✓ My family, for their never-ending support and encouraging me throughout the project. Particularly, I would like to thank my husband. Without his support, this achievement could have just been a dream.
- ✓ Chemical Industries Education and Training Authorities (CHIETA) for providing the much needed funding which enabled me to accomplish this work.
- ✓ Baker Hughes South Africa (Mossel Bay) for allowing me to make use of their facility when I carried out my cement tests. Particularly, I would like to thank Ntakadzeni Netshivhale (Field Engineer I) for her assistance in conducting the experimental work.
- ✓ The Department of Chemical and Metallurgical Engineering at the University of the Witwatersrand, including the staff and fellow students. I acknowledge all technicians, secretaries, and personnel in the department who contributed directly and indirectly to this work.

SUBMITTED MANUSCRIPTS/ CONFERENCE PUBLICATIONS

The publications emanated from this work are listed below and copies are included in Appendix B and Appendix C.

1. Kaduku, T., Daramola, M.O., Obazu, F.O. & Iyuke, S.E. (2015). Performance evaluation of South African coal fly ash- derived sodium silicate in oil well cementing operation. Southern African Institute of Mining and Metallurgy (SAIMM) Journal. (*under review*).

2. Daramola M. O., Kaduku T. & Iyuke S. E. (2015). Beneficiation of South African coal-fly ash in oil well cement operation, In: Proceedings of 1st International Conference on Oilfield Chemistry & Flow Assurance. Oilflow 2015. June 22 – 24, 2015. Port Harcourt, Rivers State, Nigeria.

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NOMENCLATURE

OWC	oil well cement
C-S-H	calcium-silica-hydrate
BWOC	by-weight-of-cement
BWOW	by-weight-of-water
BHCT	bottom hole circulating temperature
CFA	coal fly ash
CFA- Na_2SiO_3	sodium silicate synthesized from coal fly ash
com- Na_2SiO_3	commercial sodium silicate from Sigma Aldrich
WOC	wait-on-cement

CHAPTER 1: INTRODUCTION

An oil or gas well can be thousands of meters in depth and not more than a meter in diameter (Nelson and Gulliot, 1990). Oil and gas wells are normally constructed using a metal casing that is held in place by cement slurry that is poured in the void between the casing and the walls of the geological formation. Well cementing is the process of filling the void between the casing and the walls surrounding the hole with cement slurry in order to provide zonal isolation in oil, gas, and water wells (Nelson and Gulliot,1990). When the cement slurry sets, a bond is established between the casing and the formation. The aim is to prevent fluids from moving in-between zones in the well. Unsuccessful zonal isolation may result in oil spills and consequently the well may not run at its optimum production (Nelson and Gulliot, 1990).

The chemistry of oil well cement (OWC) slurries which are used for the cementing operation is more complicated compared to that of conventional cement paste. Some wells often have lost circulation zones and are prone to formation breakage. Often, low density slurries are required to overcome these problems and extenders are utilized to overcome these situations (Salim & Amani, 2013; Ahmaruzzaman 2010 and Shahriar A., 2011). The commonly used extenders are water extenders such as bentonite and sodium silicate, which allow excessive addition of water to the slurry and low density aggregates such as

microspheres and pozzolans, which have densities that are lower than that of Portland cement (3.15 $g.cm^{-3}$) (Nelson et al., 1990). These extenders reduce the density of the slurry and this results in a reduction of the hydrostatic pressure during cementing (Nelson et al., 1990). Extenders also increase slurry yield by replacing a substantial amount of cement required to complete a given task.

One of the most commonly used water extenders is Na_2SiO_3. Na_2SiO_3 is reported to be about five times more effective as an extender compared to bentonite in comparable concentrations (Nelson et al., 1990). Unlike pozzolanic extenders such as fly ash, sodium silicate is highly reactive with oil well cement (Joel and Ujile, 2009). Sodium silicate reacts with the Ca^{2+} ions from the lime in the OWC or calcium chloride to produce additional calcium-silica-hydrate (C-S-H) gel (Nelson et al., 1990). The gel structure provides sufficient viscosity to allow the use of large quantities of mix water without excessive free water separation (Nelson et al., 1990). The further C-S-H formation also results in a reduction in thickening time, and hence the accelerating effect of sodium silicate (Joel and Ujile, 2009).

The advantages of Na_2SiO_3 as an extender are its low concentration of use and high yield as compared to other extenders such as bentonite and coal fly ash (Joel and Ujile, 2009). Whilst fly ash is added in concentrations up to 50% by-weight-of-cement (BWOC) and bentonite up

to 20% BWOC, sodium silicate ranges from 0.2% to 3.0% BWOC (Nelson et al., 1990). The accelerating effect of sodium silicates, however, limits their application at lower temperatures, typically less than 52 °C bottom hole circulating temperature (BHCT) (Nelson et al., 1990; Joel and Ujile, 2009). They can be used at higher temperatures with the addition of retarders, although their effectiveness as an extender is reduced because of the inhibition of C-S-H formation (Nelson et al., 1990; Joel and Ujile, 2009).

At industrial scale, commercial sodium silicate is traditionally manufactured through calcining sodium carbonate (Na_2CO_3) and SiO_2 at temperature ranges of 1400-1500 °C in furnaces (Folleto et al., 2006). Although the raw materials are cheap, the process is not cost-effective due to its high energy consumption and maintenance cost (Folleto et al., 2006). The process also emits dust, nitrogen and sulphur oxides, contributing therefore to air pollution. Alternatively, Na_2SiO_3 can be produced through the reaction of silica with NaOH solution in an autoclave, at high temperature and pressure (McDaniel et al., 1961).

In light of the information at hand, it is necessary to carry out an investigation on alternative methods, which are less energy intensive, for producing Na_2SiO_3 for use as an additive to OWC. Against this background, this work investigated the possibility of synthesizing Na_2SiO_3 from South African coal fly-ash, a waste that is in in the country. South

Africa is mainly dependent on coal fired power stations for electricity production and about 25 million tons of ash is produced annually. This figure is yet to increase when the new Medupi and Kusile power stations, which are currently under construction, go online. Disposal of this waste constitutes a huge environmental problem at the moment.

CFA is an inorganic powder that is produced during the combustion of coal (Ahmaruzzaman, 2010). Several studies have been carried out and reported on the beneficiation of CFA (Iyer and Scott, 2001; Ahmaruzzaman, 2010; Taylor, 1990; Kamarudin et al., 2009 and Park et al., 2012). Beneficiation of fly ash from other materials such as rice husks, bagasse and corn cobs has also been reported (Aigbodion et al., 2010; Foleto et al., 2006; Okoronkwo et al., 2013). Ikotun et al (2014) analysed four South African CFAs obtained from Matla, Majuba, Lethabo and Kendal power stations and reported that all the samples had compositions typical of class F fly ash according to the ASTM C618. Similar results were reported by Ayanda et al (2012) for CFA from Matla power station and Mainganye et al (2013). Results from the aforementioned studies indicated that SiO_2 is the major component of the CFAs (50-52%). In this study, SiO_2 was extracted from CFA and used as starting material to produce Na_2SiO_3. The performance of the synthesized Na_2SiO_3 (CFA-Na_2SiO_3), as an OWC extender, was evaluated and compared with that of commercial Na_2SiO_3 (com- Na_2SiO_3).

1.1 Research Questions

The following questions were posed when carrying out this investigation:

1. Can Na_2SiO_3, an OWC extender, be produced from South African CFA at mild temperature and pressure conditions?
2. How well will the performance of the produced Na_2SiO_3 compare with the performance of a commercial Na_2SiO_3 as an OWC extender?

1.2 Aim and objectives

The aim of this study was to synthesize sodium silicate for use as an OWC extender, using mild temperature and pressure conditions; and South African CFA as a SiO_2 source.

The objectives of this study were as follows:

(i) To characterize South African coal fly ash.

(ii) To extract SiO_2 from CFA through acid leaching and use the SiO_2 to produce Na_2SiO_3.

(iii) To characterize the synthesized Na_2SiO_3 and compare the result with that of commercial Na_2SiO_3.

(iv) To prepare cement slurries with varying compositions of water, Class G Portland cement and com- Na_2SiO_3.

(v) To prepare cement slurries with varying compositions of water, Class G Portland cement and CFA- Na_2SiO_3.

(vi) To evaluate the characteristics such as density, compressive strength and rheology of the slurries prepared in (iv) and (v) and

compare results. The slurries will be tested at constant temperatures and pressure to determine the optimum operation composition.

1.3 Research benefit

South Africa is mainly dependent on coal fired power stations for electricity production and about 25 million tons of ash is produced annually. This figure is yet to increase when the new Medupi and Kusile power stations, which are currently under construction, go online. This report opens up a way for the beneficiation of South African coal fly ash in the petroleum, oil and gas industry. Furthermore, it is expected that the demand for oil in Africa will continue to escalate over the next 20 years owing to the growing population, urbanization and the mushrooming middle class with substantial income (PWC, 2014). Therefore, it is expected that unexploited oil and gas fields will become important; and South Africa, the eighth nation with recoverable gas reserves, will begin to exploit these resources (PWC, 2014). Thus, this research also contributes to the utilization of local waste in the exploration and production of oil and gas. Furthermore, the energy efficient method used in the synthesis of CFA-Na_2SiO_3 ensures energy conservation.

1.4 Scope of research and report layout

The beneficiation of CFA has been studied by many researchers and a review has been done by Iyer and Scott (2001) and Ahmaruzzaman (2010). This research work was only limited to the beneficiation of South

African CFA in oil well cementing operation. The scope of this work was to characterize CFA using different characterization techniques, extract SiO_2 from CFA and use it as a raw material for the synthesis of Na_2SiO_3. The work also included the characterization and application of the synthesized Na_2SiO_3 as an OWC extender.

This report is divided into eight chapters, including this chapter. Chapter 1 is the introductory chapter and it presents a brief overview of the importance of OWC extenders, the need to find ways for CFA beneficiation, the aims and objectives as well as the significance of the proposed study. The discussion also includes the justification on why the study was undertaken and its benefit.

Chapter 2 presents the literature review on oil well cementing, CFA and Na_2SiO_3. This includes the basic cementing process, the purpose of OWC slurry extenders, and past and recent research efforts on the use of CFA and Na_2SiO_3 in oil well cementing.

Chapter 3 presents a detailed description of the materials and methods used in this work. Its purpose is to provide information on the characterization techniques, experimental methods and raw materials used in the analysis of CFA, extraction of SiO_2 and synthesis of Na_2SiO_3. The application of the synthesized Na_2SiO_3 and evaluation of its performance is also discussed.

Chapter 4 discusses the results of the characterization of the CFA used in this study. This chapter provides useful information on the mineralogical and chemical composition of the CFA which is important in determining its potential application in this study. A comparison of these results with reports from literature is also made.

Chapter 5 presents the results of the characterization of the SiO_2 which was extracted from CFA in Chapter 3. The results are discussed and comparisons with reports from past research efforts are made.

Chapter 6 discusses the results of the comparison of the physicochemical properties of the CFA-Na_2SiO_3, synthesized in Chapter 3, and commercial Na_2SiO_3. This provides important information to ascertain the nature of the synthesized CFA-Na_2SiO_3 and determine the suitability of its use in this investigation.

Chapter 7 presents the results of the comparison between the synthesized CFA-Na_2SiO_3 and com-Na_2SiO_3 as OWC extenders. The results from the evaluation of density, compressive strength and rheology of the OWC slurries prepared in Chapter 3 are discussed. Chapter 8 provides the general conclusions drawn from this study and recommendations for future investigations.

CHAPTER 2: LITERATURE REVIEW

2.1 The Cementing process

After a well has been drilled, the drill string is removed and a casing string which is accessorized with a float collar, guide shoe and centralizers is lowered into the hole until the shoe is almost at the bottom. The cementing head, containing the top and bottom cement plugs, is attached to the upper part of the casing string. The two plug system allows passage of the cement slurry through the casing whilst reducing the contamination of the cement slurry by drilling fluids that might have remained inside the casing before the pumping of the cement slurry commenced (Nelson and Gulliot, 1990).

The bottom plug is let loose and slides inside the casing, wiping it clean. Proper removal of mud ensures that there is intimate bonding of the cement with the casing and the geological formation walls (Shahriar, 2011). The spacer is pumped in after the plug, followed by cement slurry. A spacer offers a barrier that prevents cement slurry mixing with mud (Nelson and Gulliot, 1990). On reaching the float collar, the plug's rubber diaphragm bursts, and the spacer and slurry flow through the plug, around the shoe and up the annulus. The top plug is released, followed by the displacing fluid. When the top plug lands on the bottom plug, the cementing process is completed.

The cement slurry is left to set for a time ranging from several hours to several days, and forms a stiff cement sheath which has low permeability and provides zonal isolation to the production zone from the surrounding geological formation, before the commencement of completion work or further drilling. This period of time is called wait on cement (WOC) (Nelson and Gulliot, 1990).

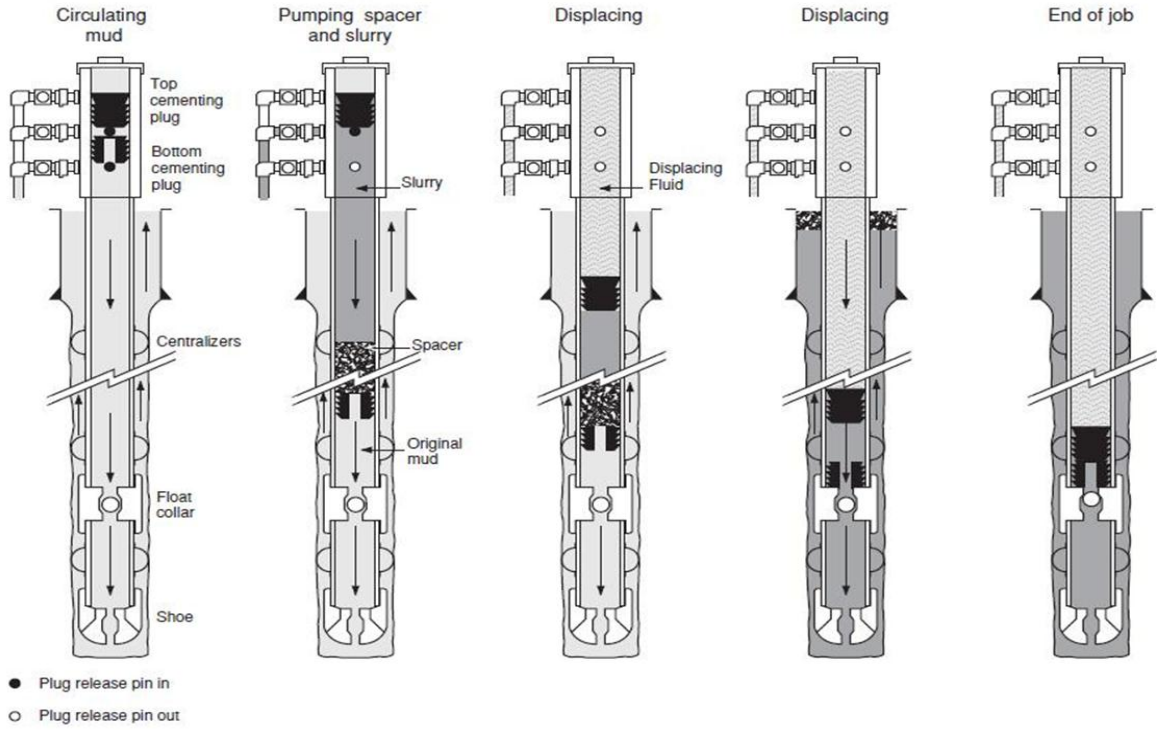

Figure 1: Single stage cementing operation (Nelson and Gulliot, 1990)

2.2 Oil well cement slurry extenders

Oil well cement slurries are designed in three different sets; namely lead slurry, critical zone slurry and the tail slurry. These slurries are designed

to meet the Texas Rail Road Commission (TRRC) Rule 13 requirements shown in Table 1 below.

Table 1: Texas Rail Road Commission Rule 13 Specifications (TRRC, 1991).

Extender Slurry		
Duration (Hours)	12	24
Compressive Strength (psi)	100	250
Tail Slurry		
Duration (Hours)	12	72
Compressive Strength (psi)	500	1200
API Free Water (ml/2hrs)	6	

The lead slurry is designed to exceed the minimum TRRC compressive and API free water requirements, whilst the tail slurry is designed for use in the critical zone (TRRC, 1991). The lead slurry is designed with the aid of extenders. Extenders are utilized to allow the use of longer columns of cement without formation collapse and for the reduction of cost of cementing material even where low density is not necessary (Nelson and Gulliot, 1990; Oriji et al., 2014). Fig 2 below shows the slurry types, and their locations in a typical cementing operation.

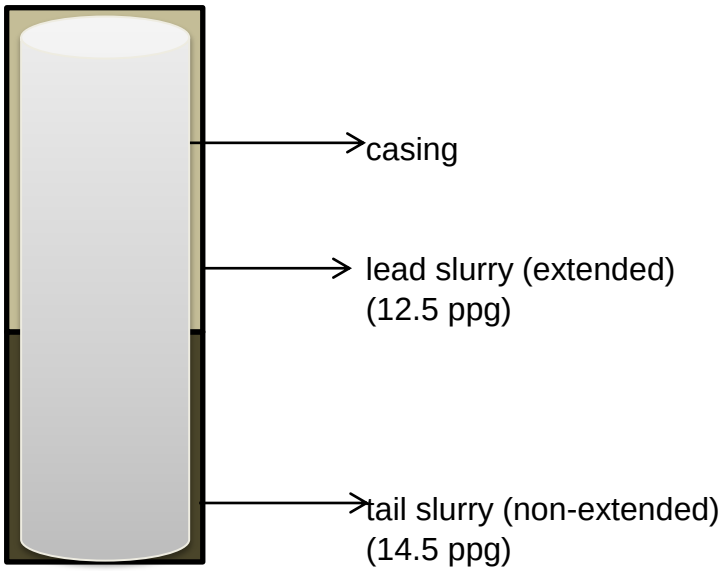

Figure 2: Typical slurry density hierarchy

There are three mechanisms of action for extenders (Odler et al*.*, 1983; Nelson and Gulliot, 1990). Low density aggregates such as microspheres and pozzolans, which have densities that are lower than that of Portland cement (3.15 g.cm^{-3}) (Nelson et al., 1990) are used to partially replace cement, thereby decreasing the overall density of the slurry. Physical and chemical extenders such as bentonite and Na_2SiO_3 absorb water, thereby allowing excessive addition of water to the slurry without producing free fluid or segregation of particles (Odler et al*.*, 1983; Nelson et al., 1990). Gases such as nitrogen are used to produce foamed cements with very low density and suitable compressive strength (Odler et al*.*, 1983; Nelson et al., 1990). These extenders reduce the density of the slurry and this results in a reduction of the hydrostatic pressure during cementing and an increase in slurry yield since they replace a substantial

amount of cement required to complete a given task (Nelson et al., 1990; Fink, 2003).

Extenders used in cement slurry design include Na_2SiO_3, clays (bentonite, attapulgite), pozzolans (coal fly ash, diatomaceous earth, condensed silica), light-weight particles (pulverized coal, gilsonite, perlite, microspheres), gases (nitrogen), among others (Nelson et al., 1990; Fink, 2003; Oriji et al., 2014). A summary of some of the OWC extenders is in Table 2.

Table 2: Typical slurry densities which are achievable when using some extenders (Nelson et al., 1990).

Extender	**Slurry Densities Achievable (g/cm^3)**
Bentonite	1.38
Gilsonite	1.44
Fly ash	1.56
Perlite	1.44
Coal	1.43
Diatomaceous earth	1.32
Sodium silicates	1.33
Microspheres	1.02
Foamed cement	0.72

2.3 CFA and its use in cementing

CFA is an inorganic powder which is produced during the combustion of coal (Ahmaruzzaman, 2010). It is made up of spherical glassy particles. (Ahmaruzzaman, 2010). It appears grey in colour and is alkaline in nature (Ahmaruzzaman, 2010). CFA is predominantly composed of small, hollow particles with particle sizes ranging from 0.01 to 200 μm (Ahmaruzzaman, 2010). Bituminous CFA has a particle size distribution that is generally less than 0.075 mm and the specific gravity of CFA usually ranges between 2.1 and 3.0. CFA has a specific surface area ranging from 170 to 1000 m^2/kg (Ahmaruzzaman, 2010).

The primary components of CFA are silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3). CFA also contains oxides of carbon, magnesium, calcium, and sulphur (Ahmaruzzaman, 2010; Iyer and Scott, 2001; Marrero et al, 2007; Van der Mwere et al, 2011). It was reported that trace and minor elements such as Ba, Ce, Cl, Cr, Cu, F, La, Mn, P, Nb, Pb, Sb, Sr, Th, Ti, U, Y, W, Zn and Zr occur as minerals and phases in fly ash (Marrero et al, 2007; Iyer and Scott, 2001). According to the American Standards for Testing Materials (ASTM C618) specifications, three types of fly ash are recognized: types N, F and C (Nelson et al, 1990) (see Table 3).

Table 3: Classification of fly ashes (Nelson et al, 1990).

Mineral Admixture Class	N	F	C
$SiO_2 + Al_2O_3 + Fe_2O_3$, min. %	70	70	50
SO_3, max. %	4	5	5
Moisture content, max. %	3	3	3
Loss on ignition, max. %	10	12	6

Some derivatives of CFA have been reported to be used in the preparation of lightweight cement for oil wells. Bierderman, (1972) formulated an oil well cement composition utilizing hollow cenospheres of float ash which is produced from CFA. Float ash is the portion of CFA which floats on water and exhibits a specific gravity of about 0.7 (Bierderman, 1972). The lightness of the float ash and its inherent compressive strength make it quite suitable for use as an additive that decreases the weight of OWCs (Bierderman, 1972).

CFA has also been reported as a source of silica (Taylor, 1990; Kamarudin et al, 2009 and Park et al, 2012) along with other materials such as rice husk ash (Foleto et al., 2006), bagasse ash (Aigbodion et al., 2010) and corn cob ash (Okoronkwo et al., 2013). Silica is added to OWC to inhibit strength retrogression at elevated temperatures (Velez et al, 1996; Anjos et al, 2010). Strength retrogression is the extent at which compressive strength decreases and permeability increases as the curing time of the cement progresses (Taylor, 1990). The calcium silicate hydrate (C-S-H) which is produced during the hydration of Portland

cement is primarily responsible for the resultant mechanical strength of the hardened cement and the physical and chemical stability at temperatures up to 110 ^{o}C (Souza, 2012). At higher temperatures, there is a high formation of crystalline silicate hydrates, such as C_3S-$H_{1.5}$ and C_2S-H (Jupe et al., 2007). These hydrates negatively affect the mechanical properties of the slurry (Jupe et al., 2007), and silica inhibits their formation.

CFA has found an important use as an OWC extender. When CFA is used as partial replacement for Portland cement, its spherical particle shape and relatively low specific surface area reduces the slurry's water demand (Shahriar A., 2011). This results in a reduction in the density of the slurry. The use of CFA as an extender however has shortcomings. Increasing the amount of CFA in OWC results in slower strength gain and longer setting times (Bazzar et al, 2013). This results in low early-age strength and delays in the well completion process. Against this background, in this study, a decision was made to use a derivative of CFA to synthesize a possibly more effective extender which has higher early-age strength and shorter setting time compared to CFA.

2.4 Sodium silicate- an OWC extender

Sodium silicate is obtainable in both solid and liquid forms. This makes it suitable and adaptable for use in both offshore and onshore operations. Solid sodium metasilicate (Na_2SiO_3) is normally dry-blended with cement.

For direct dissolution in water, sea water is preferable and when fresh water is used, $CaCl_2$ is first dissolved in the water. The $CaCl_2$ aids the formation of a gel when Na_2SiO_3 is dissolved in water. The liquid form of sodium silicate is a silicate polymer containing three to five silicate molecules in the chain (Na_2O. (3–5)SiO_2). Sodium silicates containing more than five silicate molecules are not effective as chemical extenders because of their reduced solubility (Nelson et al., 1990; Joel and Ujile, 2009). The structural formula of sodium metasilicate is shown in Fig 3.

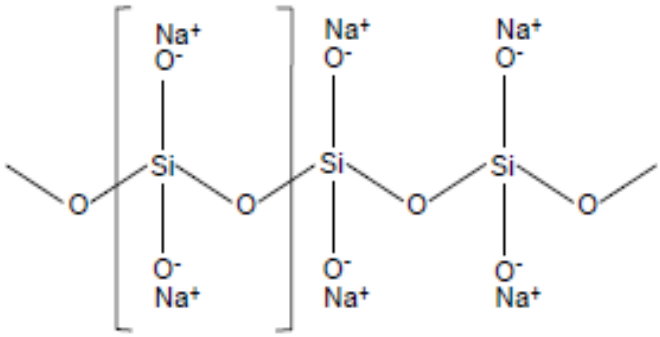

Figure 3: Structural formula of sodium metasilicate.

Not only is Na_2SiO_3 used as an extender for oil well cement slurries, it has an accelerating effect as well (Nelson et al., 1990). Malyshev et al., (2013) reported on the use of Na_2SiO_3 as an OWC extender for a lightweight cement system of density 1500 kg/m^3 (12.6 ppg). Fasesan, (2005) undertook a study to determine the viability of substituting 2 % (BWOC) bentonite, which is usually added in 50:50 Class H (or Class C): Pozzolan slurries with 0.5 % (BWOC) Na_2SiO_3 and reported that the small quantity of Na_2SiO_3 effectively replaces bentonite and controls free water formation at the same degree as the bentonite.

Fasesan, (2005) also reported that unlike bentonite, which reduces the effectiveness of a given concentration of most commercially available fluid loss additives in typical cement slurries, Na_2SiO_3 worked well with a commonly available fluid loss additive. Furthermore, the use of small quantities of Na_2SiO_3 (0.5 % BWOC) to replace bentonite (2 % BWOC), significantly reduces the shipping costs associated with moving tons of the material over a long period of time (Fasesan, 2005). Vipulanandan et al, (2014) evaluated the behaviour of oil well cement with and without Na_2SiO_3 up to 0.3% from curing to hardened state and reported that addition of 0.2% Na_2SiO_3 increased the yield strength, viscosity, and fluid loss, and had no effect on compressive strength of the cement.

Furthermore, Na_2SiO_3 has been reported to be synthesized from CFA (Folleto et al, 2006; Kamarudin et al, 2009). Folleto et al, (2006) successfully produced Na_2SiO_3 through the alkali leaching of rice hull ash using sodium hydroxide solution. In this study, SiO_2 was extracted from CFA and used as starting material to produce Na_2SiO_3. The performance of the synthesized CFA-derived Na_2SiO_3 as an OWC extender was evaluated and compared with that of the commercial Na_2SiO_3.

CHAPTER 3: EXPERIMENTAL PROCEDURE

This chapter focuses on the analytical and experimental equipment and methods used in this study. The investigation was divided into four stages;

(i) Characterization of CFA.

(ii) Extraction and characterization of SiO_2.

(iii) Synthesis and characterization of Na_2SiO_3.

(iv) Preparation and characterization of OWC slurries extended with Na_2SiO_3.

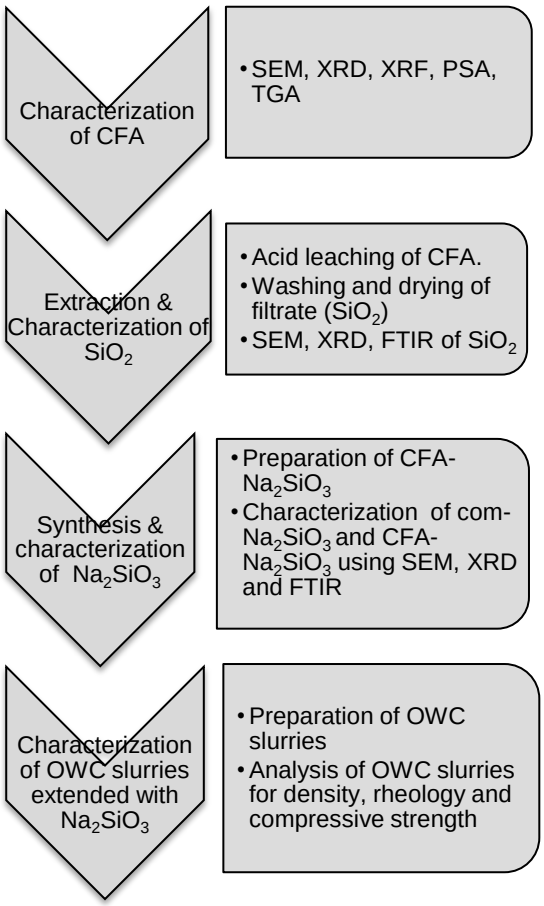

Figure 4: Flow chart of experimental work carried out in the study.

3.1 CFA Sampling

A grab sample of South African CFA was collected from Power Station X, in South Africa. Small quantities of CFA were scooped randomly from different points and then mixed together to make the representative sample. This sampling method ensures that the sample is quickly collected and sealed away. This is done to reduce the error introduced by exposing the material for a longer time, which occurs when other elaborate sampling methods are used (Wills and Napier-Munn, 2005). A detailed mineralogical examination using X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), proximate and particle size analysis was carried out on the CFA sample.

3.2 Characterization techniques

For qualitative and quantitative analyses of CFA, extracted SiO_2, CFA-Na_2SiO_3 and com-Na_2SiO_3 a Brucker D2 X-ray Diffraction machine was used. The samples were crushed and subsequently milled to very fine powder (<10µm) using an automatic grinder, to be suitable for quantitative XRD analysis. In order to determine the non-crystalline content of the samples, an internal standard (CaF_2) was added to the samples. The samples were then subjected to X-ray diffraction.

To determine the elemental compositions of the CFA a PANalytical AXIOS X-Ray Fluorescence (XRF) Spectrometer was used. Each sample was ground to 100% passing 212 µm. The samples underwent calcination

at 850°C in air for 4 h for the removal of all organic material and water. The samples were then fused with lithium tetraborate ($Li_2B_4O_7$). The prepared solid solution and a standard were placed in the sample holder. The sample holder was placed in the XRF spectrometer for analysis. The concentration of the element in the samples was calculated from the intensity of the characteristic line of the element.

The morphologies of the CFA, extracted SiO_2, CFA-Na_2SiO_3 and com-Na_2SiO_3 were analysed using a ZEISS Sigma VP Field Emission-SEM machine. The samples were first sputtered with a double coat of gold and palladium, 10 µm thick. The sputter coating gives the samples the advantage of increased thermal conduction, reduction in microscope beam damage and reduced charging. The coated samples were then placed in the SEM machine where a microscope scanned a focused electron beam over their surface and created images with varying magnifications.

To carry out proximate analysis on the CFA sample a TGA DSC STA 600 with Pyris software was used. The purpose was to determine moisture content, loss of ignition (LOI) and amount of volatiles in the CFA. Firstly, a crucible was tarred to zero at 30 °C. A sample weighing approximately 11 mg was put in the crucible and gently lowered into the furnace using a pair of tongs. The sample weight was normalized and the proximate analysis program was run. When the program finished running, the

crucible was removed from the furnace using a pair of tongs and cooled in a desiccator.

The pH of CFA dissolved in water was measured using a Metrohm 744 pH meter. 100 g of CFA was added to 1000 ml de-ionized water at 25 °C. The slurry was stirred using a magnetic stirrer at 250 rev/min. The change in pH of the slurry was monitored at 1 minute intervals until it became constant.

A Mastersizer 2000 was used to determine the particle size distribution of the CFA. A sample of CFA was wetted using de-ionized water. The CFA was dispersed in the de-ionized water and an ultrasound was used to ensure complete dispersion. Once full dispersion had been achieved, the ultrasound probe was switched off and the particle size was monitored.

The purity of the amorphous SiO_2 extracted from CFA, CFA- Na_2SiO_3 and com- Na_2SiO_3 was analyzed using a Brüker Tensor 27 Fourier Transform Infrared spectrometer. The spectra were recorded in the range of 500-2500 cm^{-1}.

3.3 Extraction of silica from CFA

The metal oxides such as alumina and calcium oxide were removed from CFA through acid refluxing using 3M HCl. For every 9 g of CFA, 120 ml of HCl solution was used. The reflux was carried out at 100 °C for 6 hours (Tang et al, 2012). Through filtration, the solid product (SiO_2) was separated from the liquid. Purification of this SiO_2 for removal of impurities

constituted successive demineralized water washings. Wet SiO_2, after removal of impurities, was dried in an oven at 200 °C for 2 hours to obtain an amorphous SiO_2 powder. 100 g of CFA yielded 24 g of SiO_2. The SiO_2 was then subjected to XRD, SEM EDS and FTIR analyses.

3.4 Preparation of CFA-Na_2SiO_3

60 g of the extracted SiO_2 was reacted with 80 g NaOH pellets in 100 ml distilled water to produce sodium silicate solution. This reaction was carried out in a Pyrex flat bottomed flask at 80 °C and atmospheric pressure. 100ml distilled water was poured into the flask and placed on a heating mantle equipped with a magnetic stirrer and heated to 40 °C. 80 g NaOH pellets were slowly added to the water and stirred continuously until they melted. A temperature increase of 40 °C was observed as the pellets dissolved. Thereafter, the amorphous SiO_2 powder was slowly added to the solution and continuously stirred at 80 °C until a homogenous solution was obtained. The homogenous solution was stirred for a further 30 minutes at 80 °C to ensure a complete reaction.

The colourless viscous solution was then poured into a crucible and calcined at 300°C for 3 hours to get rid of NaOH and water. A white solid was obtained and crushed using a mortar and pestle to make Na_2SiO_3 powder. The product was then subjected to SEM EDS, XRD and FTIR analyses.

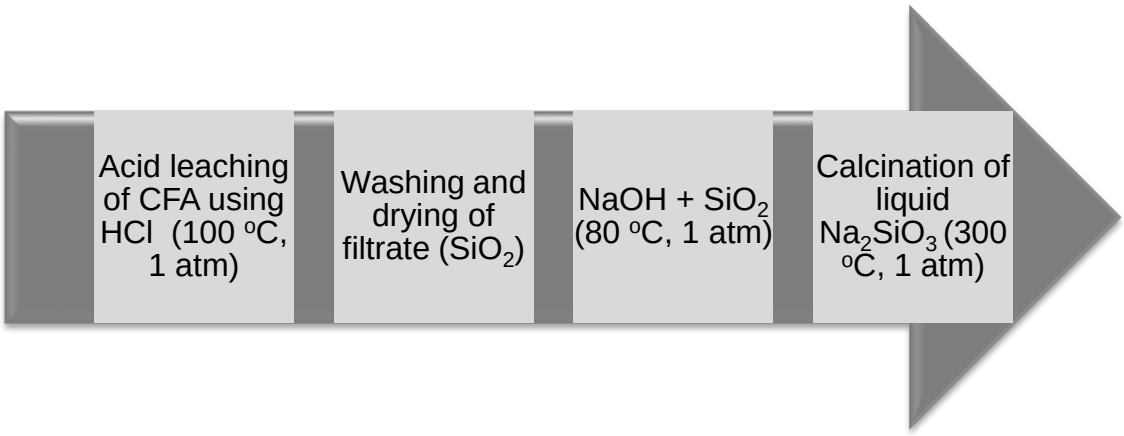

Figure 5: Flow diagram of synthesis of Na_2SiO_3 using CFA.

3.4 Preparation of OWC slurries

Slurries with varying compositions of cement, water, CFA- Na_2SiO_3 and com- Na_2SiO_3 were prepared. The slurry compositions are shown in Table 4. Distilled water containing 2 % $CaCl_2$ by-weight-of-water (BWOW) was used at a temperature of 23 ^oC. $CaCl_2$ was first dissolved in the water to improve the efficiency of sodium silicate. The slurry mixing was carried out in a Chandler Ametek Constant Speed Mixer Model 30-60 in accordance with the specification for materials and testing for Well Cements (API, 1990).

Table 4: Compositions of the prepared OWC slurries

% Additive	% $CaCl_2$	% Water	Class G Cement (g)
0	2	44	792
0.25	2	68	677
0.5	2	78	638
0.75	2	104	555
1	2	78	637
1.5	2	80	627
2	2	88	595
2.5	2	100	556

3.5 Characterization of OWC slurries

The slurries were pre-conditioned using an Atmospheric Consistometer prior to the rheology test. The consistometer is made up of a rotating cylindrical container which has a stationary paddle inside, in a temperature controlled bath. The bottom hole circulating temperature (BHCT) used for the rheology tests was 52 ^{o}C. The slurry was stirred for a period of 20 minutes at a speed of 150 rpm.

Parameters of the slurries such as shear thinning, plastic viscosity, apparent viscosity and yield stress were studied. The viscosity of the slurries was measured using a Chandler Ametek automated viscometer Model 3530. Measurements were recorded at ambient temperatures and BHCT conditions of 52 ^{o}C.

To determine the densities of the slurries a pressurized mud balance was used. This was done to ensure that any entrained air is removed before measuring the density of the slurry.

According to API specifications, 500 psi is the minimum compressive strength needed for holding a casing and sealing the formation. The Ultra Sonic Cement Analyzer (UCA) was used to determine the development of compressive strength of the cement slurries. In this test, sonic speed was measured through the cement as it sets and the value was converted into compressive strength, in pounds per square inch (psi). The strength development was observed at BHCT of 52 ^{o}C and pressure of 5000 psi.

CHAPTER 4: PHYSICO-CHEMICAL PROPERTIES OF CFA

4.1 Introduction

It is important to study the mineralogy of CFA in order to relate it to its intended applications and to ascertain any possible environmental impacts. The physicochemical properties of CFA differ greatly depending on the type of coal, the operating conditions of the boiler utilized and the combustion conditions. This chapter discusses the results obtained from the characterization of CFA from Power Station X using XRD, XRF, SEM, TGA and PSA. A comparison of the results from this study with results previously reported in literature is also made.

4.2 Crystallinity of CFA using XRD

Figure 6 shows the XRD patterns for the CFA. The patterns show that the dominant phases are mullite Al(Al1.272Si0.728O4.864) and quartz alpha (SiO_2). Small quantities of magnesium oxide (MgO_4), lime (CaO) and iron oxide (epsilon-Fe_2O_3) were also identified. The same phases were identified in previously studied South African CFAs (Ayanda et al, 2012, Mainganye et al, 2013 and Ikotun et al, 2014). Better understanding of the quantities of these phases was obtained with XRF analysis.

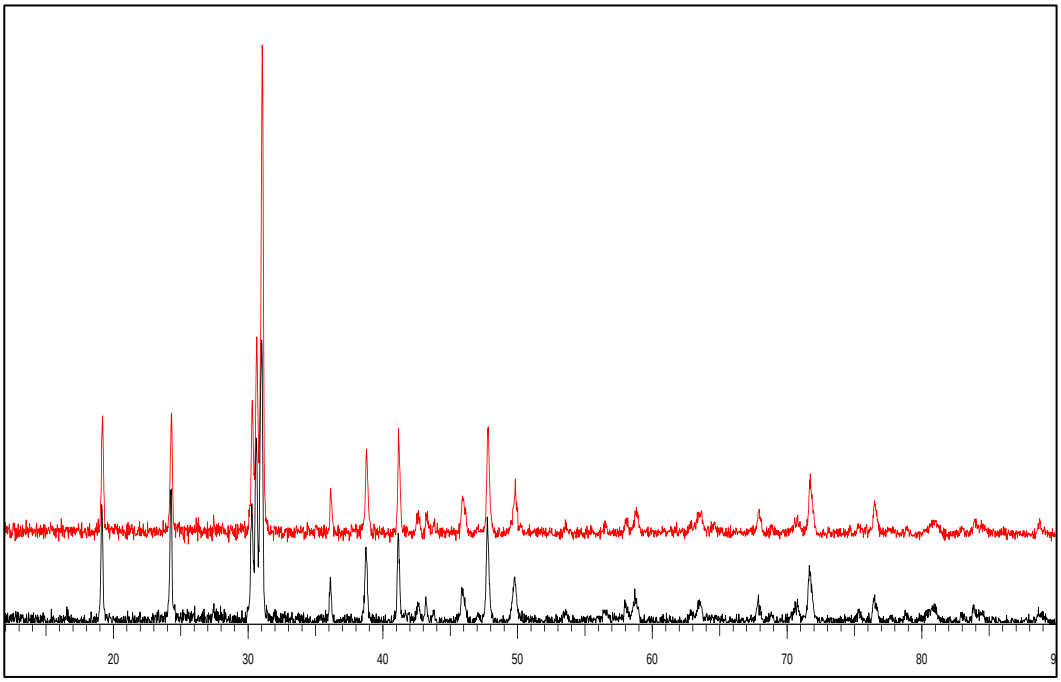

Figure 6: XRD diffractogram of two samples of CFA

4.3 Elemental composition of CFA using XRF

Table 5 shows the XRF results of the CFA from Power Station X compared with reports from literature (Ayanda et al, 2012; Mainganye et al, 2013). The analysis showed that the major components of the CFA from Power Station X are silica, alumina, iron oxide, calcium oxide and carbon (inferred from the Loss on Ignition (LOI) test). The results showed that Power Station X CFA is class F (ASTM C618, 2012) and the order of the metal oxides decreases in the order SiO_2> Al_2O_3> Fe_2O_3> CaO> MgO> K_2O> Na_2O> TiO_2. This order is consistent with previous reports on South African CFA (Ayanda et al, 2012; Mainganye et al, 2013; Ikotun et al, 2014). Interestingly, the CFA contains about 58 % SiO_2, a desired component for the synthesis of Na_2SiO_3.

Table 5: XRF analysis of CFA from Power Station X compared with literature

Element	% Composition Power Station X CFA	Mainganye et al. 2013	Ayanda et al. 2012
SiO_2	57.9	55.66	51.43
Al_2O_3	31.12	27.95	30.93
Fe_2O_3	0.33	3.22	2.29
FeO	2.65	NR	NR
MnO	0.04	0.04	0.02
MgO	0.95	1.91	1.95
CaO	4.28	4.38	6.75
Na_2O	0.13	0.31	0.54
K_2O	0.66	0.48	0.77
TiO_2	1.519	1.13	1.74
P_2O_5	0.39	0.26	1.08
Cr_2O_3	0.0223	0.03	0.02
NiO	0.0008	NR	0.01
LOI	0.73	4.74	1.21
Sum %	**100.72**	**100.07**	**99.28**

4.4 Morphology of CFA using SEM

The morphology of the CFA is depicted in the SEM micrographs in Fig 7. The shapes of the CFA particles are determined by their exposure conditions (time and temperature) in the combustion chamber (Fisher et al, 1978). As seen in Fig 2, most of the particles are spherical, as seen at higher magnifications. A similar observation has been reported by Ayanda et al, 2012 and Mainganye et al, 2013. The particles are a mixture of opaque and non-opaque spheres. The opaque spheres are predominantly iron oxides and some silicates whilst the non-opaque spheres are mainly silicates (Fisher et al, 1978). Previous studies have shown that fly ash is

made up of, in some cases, smaller particles which are attached to the surface of larger particles, hollow spheres (cenospheres), and some spheres containing other spheres (plerospheres) (Mainganye et al, 2013). In addition, the SEM micrograph shows the presence of some non-spherical particles. These amorphous particles which are non-spherical mainly arise from incomplete combustion of coal components due to less exposure to high temperatures (Fisher et al, 1978).

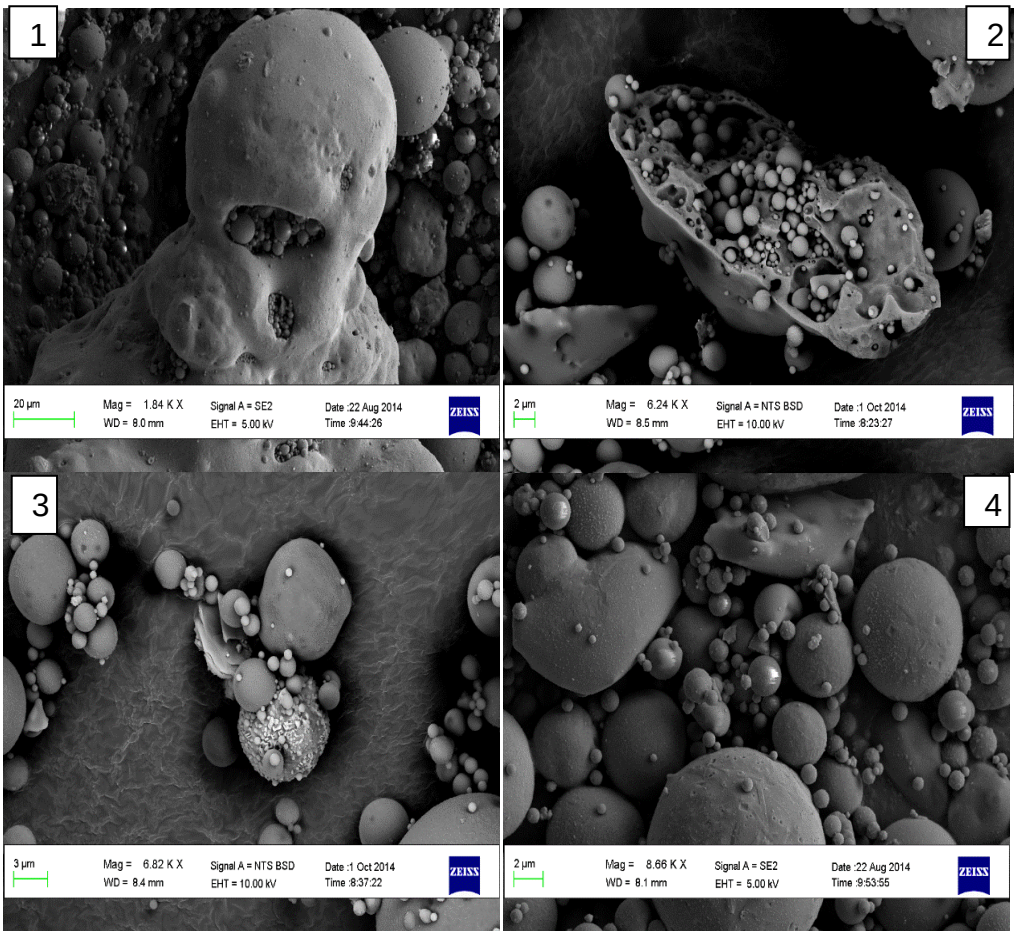

Figure 7: SEM micrographs of CFA from power station X

4.5 Proximate analysis, particle size and pH of CFA

The TGA conducted on the CFA shows that the CFA contains about 0.2% moisture, 1.6% volatile matter and 1.7% fixed carbon (Fig 8). The particle size analysis shows that the particle size of CFA ranges from 0.32 – 112 µm (Fig 9). The results are in agreement with previous studies as well (Ayanda et al, 2012, and Ikotun et al, 2014). A rise in pH from 7 to 10.7 was observed when the CFA was mixed with de-ionized water over a period of 5 hours. The increase in the pH could be attributed to the dissolution of compounds such as CaO in the CFA. This observation is in good agreement with the report by (Ayanda et al, 2012).

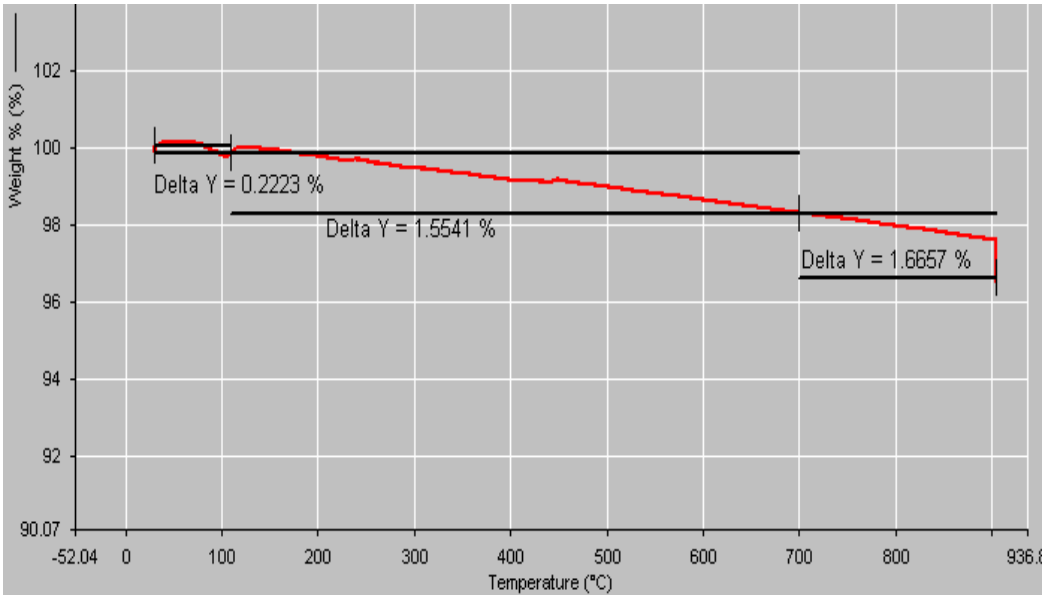

Figure 8: TGA results of CFA from Power Station X

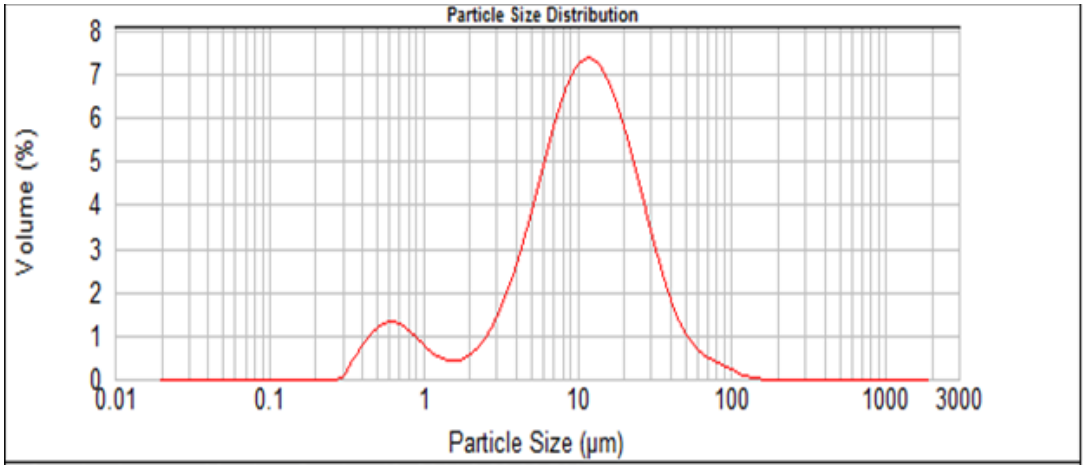

Figure 9: Particle size distribution profile of CFA from power station X.

4.6 Summary

The results obtained from the analysis showed that South African CFA from Power Station X is Class F (ASTM C618, 2012) and contains 58% amorphous SiO_2 , which is the desired component in this study. This CFA falls in the same class as some previously studied non- South African CFAs (Bayat, 1997; Sarkar et al, 2005). Moreover, the high SiO_2 content makes it most suitable for this particular study.

CHAPTER 5: CHARACTERIZATION OF SiO_2 EXTRACTED FROM CFA

5.1 Introduction

In order to determine whether the material extracted from the CFA through acid leaching was SiO_2, an analysis of its physicochemical properties was carried out. This chapter focuses on the results obtained for the characterization of the extracted SiO_2. The SiO_2 was analysed using SEM, XRD and FTIR techniques. A comparison of the results from this study with results previously reported in literature is also made.

5.2 Morphology of the extracted SiO_2 using SEM

The morphology of the extracted SiO_2 was checked with SEM using the method described in Chapter 2. Figure 10 shows an SEM image of the silica extracted from CFA (left), which is similar to that of precipitated silica (right) taken from literature (Music et al, 2011). The elemental compositions obtained using EDX showed Si and O, indicating the presence of SiO_2.

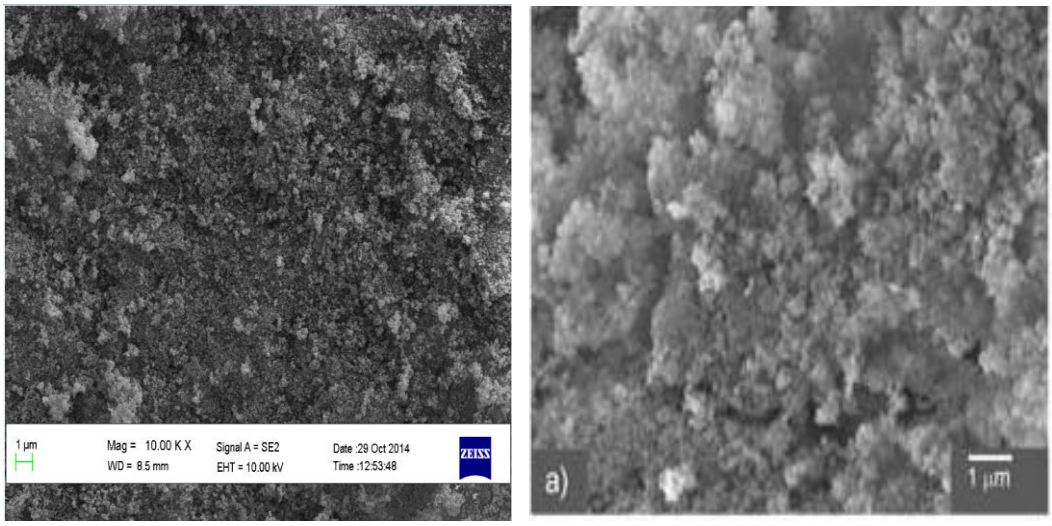

Figure 10: SEM micrograph for amorphous silica extracted from CFA (left) and SEM micrograph of precipitated silica (right) (Music` et al, 2011).

5.3 Crystallinity of the extracted SiO_2 using XRD

The XRD pattern in Fig 11 shows the characteristic slope and pattern for amorphous SiO_2. The pattern is a broad band with a peak which indicates that the substance is amorphous and contains pure SiO_2 (Saikia et al, 2008; Essien et al, 2011, Music et al, 2011 and Okoronwo et al, 2013). Similar patterns for amorphous silica have been recorded in literature (Saikia et al, 2008 and Okoronwo et al, 2013). The two sharp peaks on the pattern are due to the presence of quartz, corroborating the results obtained from EDX.

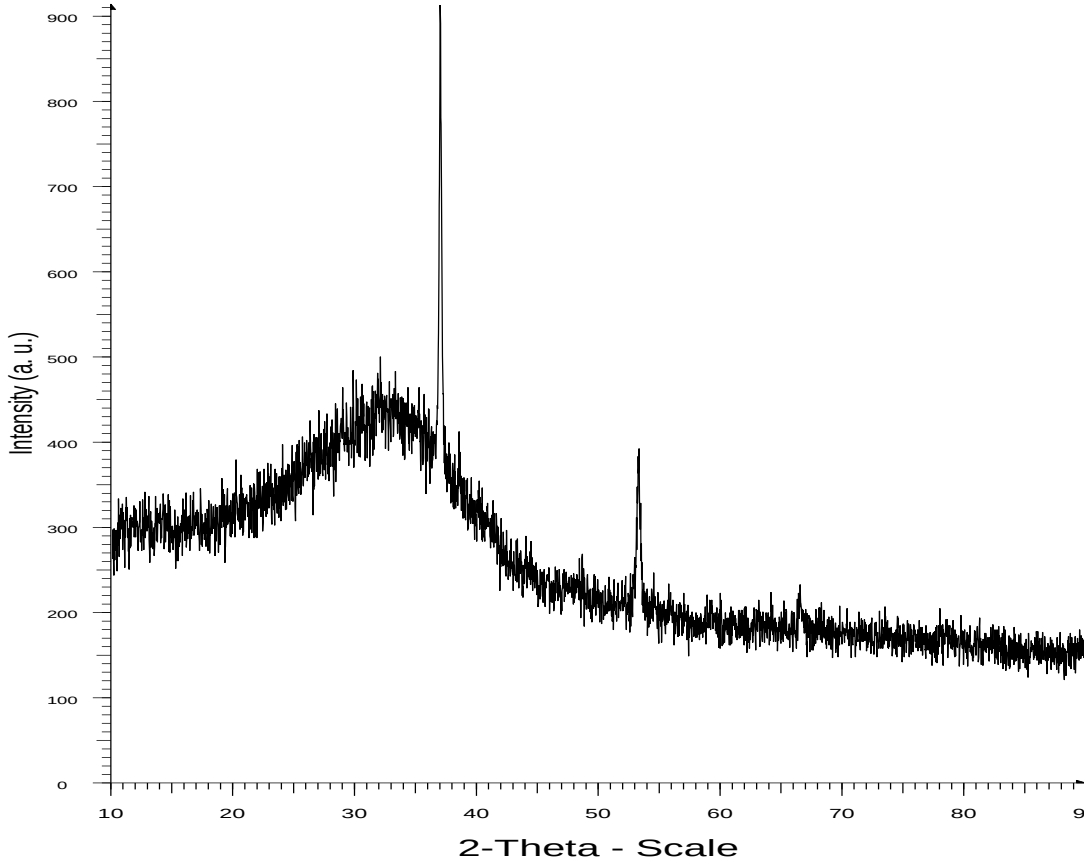

Figure 11: XRD patterns of the extracted silica from CFA

5.4 Purity of the extracted SiO_2 using FTIR

Purity of the extracted SiO_2 was checked with FTIR. The FTIR spectrum of the SiO_2 is depicted in Fig 12. The bands of absorption at 1199 cm^{-1}, 964 cm^{-1} and 682 cm^{-1} can be attributed to the absorption peaks characteristic of SiO_2 (Ying-Mei et al, 2010). Absorption peak at 1199cm^{-1} corresponds to the asymmetrical stretching vibration of Si – O (Ying-Mei et al, 2010). In addition, absorption peaks at 964 cm^{-1} and 682 cm^{-1} correspond to the symmetrical stretching vibrations of Si – O groups on the surface of the amorphous solid (Ying-Mei et al, 2010; Essien et al,

2011). The stretch between 1500 cm^{-1} and 2000 cm^{-1} can be attributed to the presence of the Si–OH and bending vibration absorption of the O–H bond of physically adsorbed water respectively (Music et al, 2011).

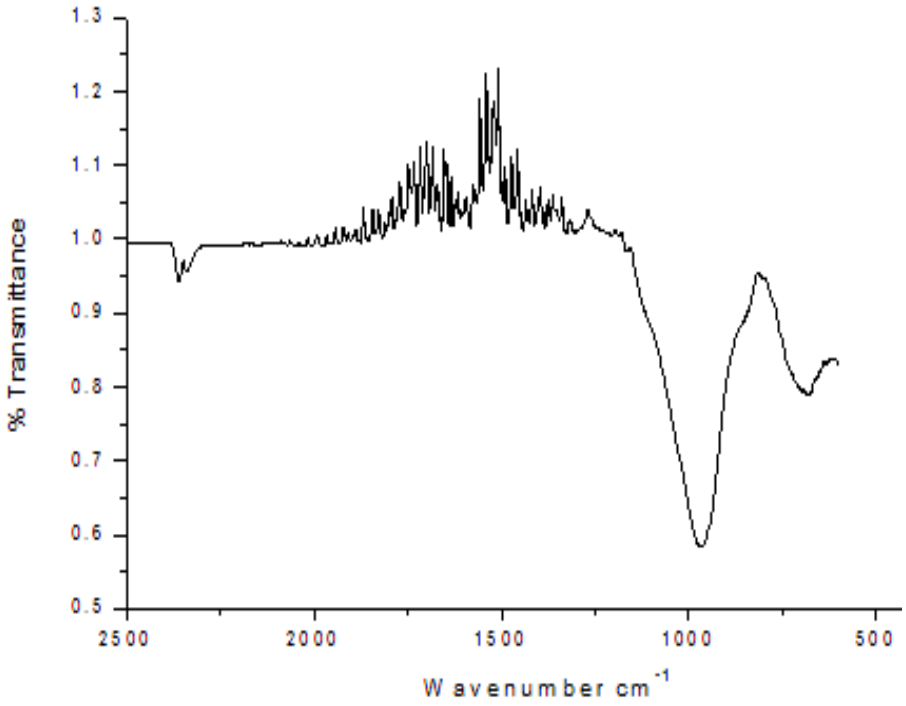

Figure 12: FTIR spectra of the extracted silica from CFA

5.5 Summary

The results show that SiO_2 was successfully extracted from CFA through acid leaching. The SiO_2 extracted is amorphous in nature, with traces of crystalline quartz. 100 g of CFA yielded 24 g of SiO_2. Thus the yield using this method is 41 %.

CHAPTER 6: PHYSICO-CHEMICAL PROPERTIES OF SYNTHESIZED Na_2SiO_3

6.1 Introduction

In order to ascertain if the product obtained from reacting the extracted SiO_2 and NaOH in Chapter 3 Na_2SiO_3, the physicochemical properties of the product were analysed. Commercial Na_2SiO_3 purchased from Sigma-Aldrich was used as a standard for comparison. This chapter focuses on the results obtained from the comparison between samples of Na_2SiO_3 prepared using the SiO_2 extracted from CFA and commercial Na_2SiO_3. The samples were analysed using XRD, SEM and FTIR techniques.

6.2 Morphology of the synthesized CFA-Na_2SiO_3 using SEM

Figure 13 depicts the SEM images for CFA-Na_2SiO_3 and com- Na_2SiO_3. The morphology of the CFA-Na_2SiO_3 is totally different from that of com-Na_2SiO_3. However, the EDX show the same elemental components with different compositions. The difference in the morphologies could be attributed to the processes used for preparing the two sodium silicates. CFA-Na_2SiO_3 is prepared using a wet process and moisture is driven out in an oven at 200 ^oC whilst com- Na_2SiO_3 is prepared using a dry process at temperatures ranging between 1400- 1500 ^oC.

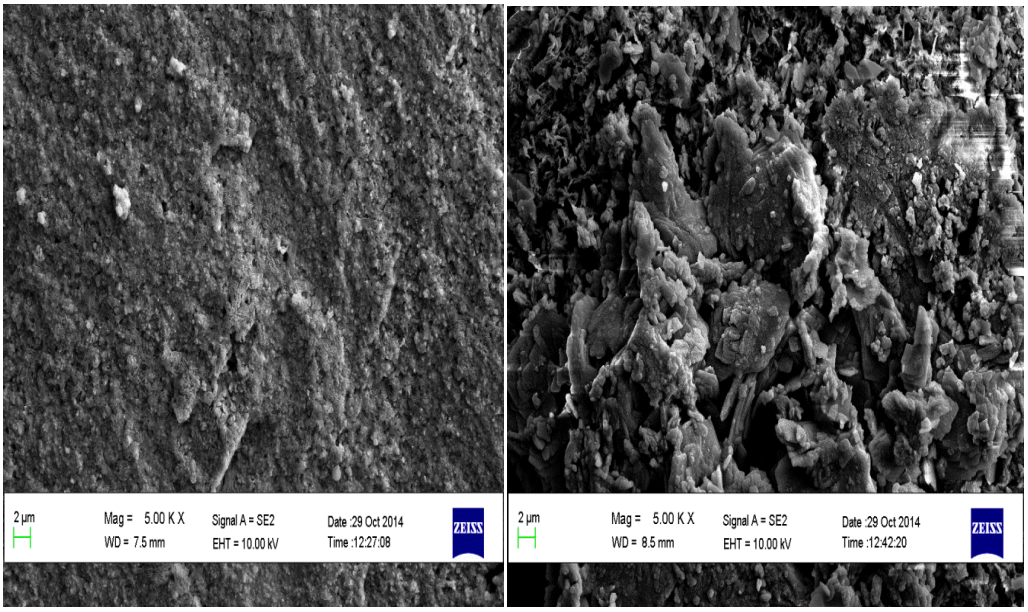

Figure 13: SEM micrographs for commercial sodium silicate (left) and CFA- sodium silicate (right).

6.3 Crystallinity of the synthesized CFA-Na_2SiO_3 using XRD

The XRD patterns for CFA-Na_2SiO_3 and com-Na_2SiO_3 are shown in Fig. 14. The two patterns are similar although a little difference in the intensities of some of the peaks was observed. Curve fitting showed that there is a slight shift in the peaks of CFA-Na_2SiO_3. The shift in the peaks could be attributed to the small quantity of the sample used in the analysis.

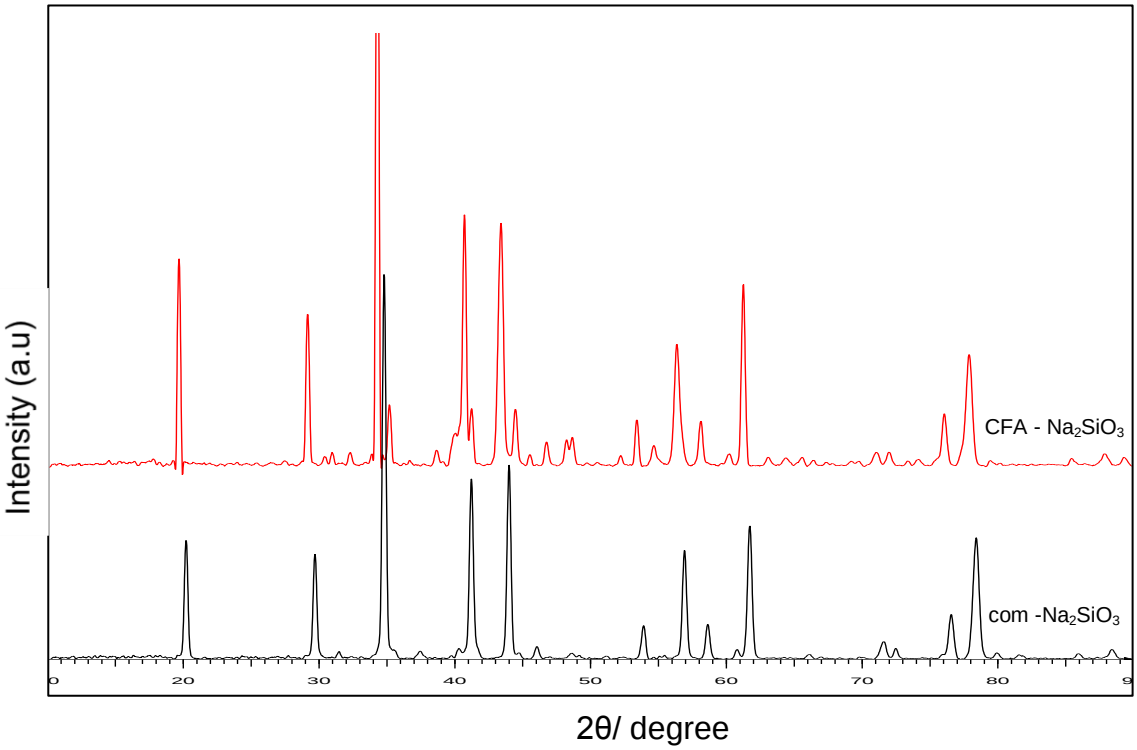

Figure 14: XRD diffractograms for commercial sodium silicate and CFA sodium silicate.

6.4 Purity of the synthesized CFA-Na_2SiO_3 using FTIR

Figure 15 shows the IR spectra of CFA-Na_2SiO_3 and com- Na_2SiO_3. The FTIR analysis of the two samples indicates that there is no observable chemical difference in the samples. FTIR of both samples show absorption bands at 2340 cm^{-1}, 1160 cm^{-1}, 1125 cm^{-1}, 980 cm^{-1}, and 715 cm^{-1} that characterize the presence of Na_2SiO_3 (Miller and Wilkins, 1952). The stretch between 1500 cm^{-1} and 2000 cm^{-1} could be attributed to the presence of the Si–OH and bending vibration absorption of the O–H bond (Ying-Mei et al, 2010).

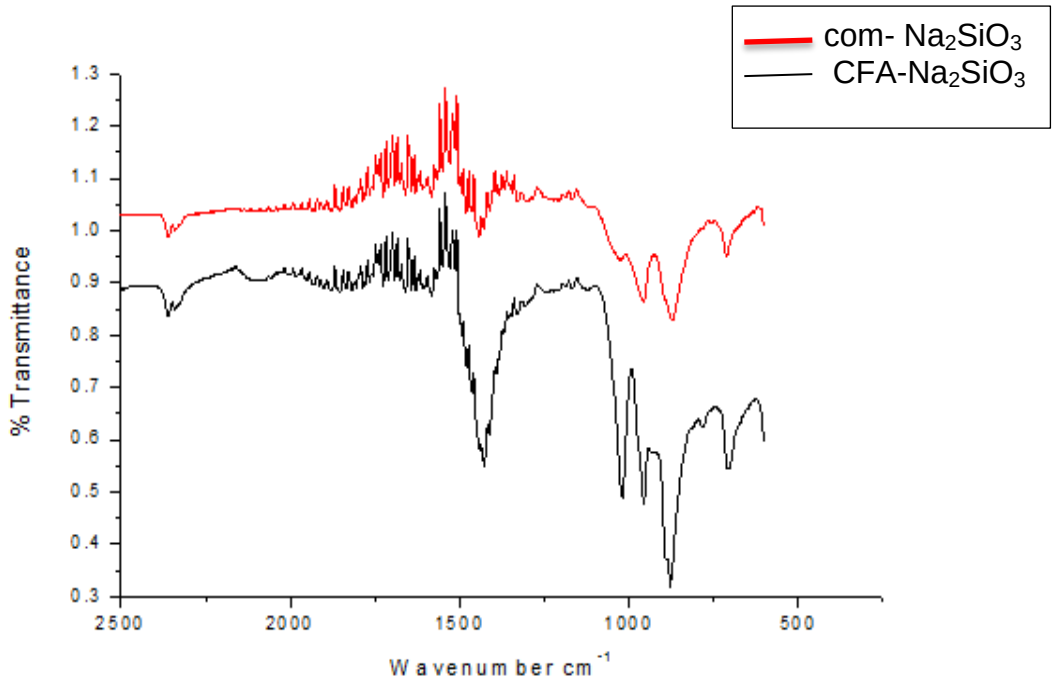

Figure 15: FTIR Spectra of CFA-Na_2SiO_3 and com-Na_2SiO_3.

6.5 Summary

The results show that CFA-Na_2SiO_3, which has similar physico-chemical properties as the commercial Na_2SiO_3, can be synthesized using SiO_2 that was extracted from CFA using mild temperature and pressure conditions. The possibility of energy saving when using this method could make it very attractive in comparison to the traditional energy-intensive method.

CHAPTER 7: USE OF THE SYNTHESIZED CFA-Na_2SiO_3 AS AN OWC EXTENDER

7.1 Introduction

The aim of this study was to synthesize sodium silicate for use as an OWC extender, using mild temperature and pressure conditions and South African CFA as a SiO_2 source. The performance of the synthesized CFA-Na_2SiO_3 as an OWC extender was evaluated and compared to that of commercial Na_2SiO_3. This chapter focuses on the results from the comparative study to evaluate the performance of OWC slurries extended using com-Na_2SiO_3 and CFA-Na_2SiO_3. Parameters considered were density, compressive strength, and rheology and all tests were done according to API Specifications 10B.

7.2 Densities of the extended OWC slurries

The compositions and the densities of the slurries prepared using CFA-Na_2SiO_3 and com-Na_2SiO_3 as additives are shown in Table 5. The slurries had similar densities with slight differences as the amount of additive added increases. Some of the slurries containing CFA-Na_2SiO_3 had slightly lower densities compared to the slurries containing com-Na_2SiO_3. There was a 0.02 % difference in the densities of the slurries containing 2 % additive. The difference may be because slurries prepared using CFA-Na_2SiO_3 had a lot of froth.

Table 6: Compositions and densities for OWC slurries

% Additive	Water (%)	Class G Cement (g)	Slurry density (ppg) (Na_2SiO_3)	Slurry density (ppg) (CFA Na_2SiO_3)
0	44	792	15.8	15.8
0.25	68	677	14.0	14.0
0.5	78	638	13.4	13.5
0.75	104	555	12.5	12.4
1	78	637	13.5	13.4
1.5	80	627	13.1	13.0
2	88	595	13.0	12.8
2.5	100	556	12.8	12.6

7.3 Rheologies of the extended OWC slurries

Rheologies of slurries prepared using CFA-Na_2SiO_3 and com- Na_2SiO_3 as additives are shown in Tables 6 and 7, respectively. The slurries prepared using both additives exhibited good rheologies with plastic viscosities (P_v) between 3.75 and 18.75 cp and yield points (Y_p) between 13.5 and 61.75 lb/100ft^2. The slurries containing com-Na_2SiO_3 generally had higher rheological values compared to those prepared using the CFA-Na_2SiO_3. At 60 rpm the viscosity of the slurry containing 1% com-Na_2SiO_3 was 45 cp whilst that for the CFA-Na_2SiO_3 slurry was 26 cp. The slurries prepared using CFA-Na_2SiO_3 were less viscous and this can be attributed to the presence of froth.

Table 7: Rheologies of slurries prepared with commercial sodium silicate.

Rheology @ BHCT (rpm)	% SS 0.25	0.5	0.75	1	1.5	2	2.5
300	29	42.5	21.5	59	76	64	70
200	24.5	37	18.5	52	70.5	59	67.5
100	24	33	19	46.5	64	56	64.5
60	23	31.5	19	45	60	56	63
30	22	30	19.5	23.5	56	54	55.5
6	15	19	14	23	32	38.5	33
3	12	12	11.5	20	26	27	29.5
P_v (cp)	7.5	14.25	3.75	18.75	18	12	8.25
Y_p (lb/100ft^2)	21.5	28.25	17.75	40.25	58	52	61.75

Table 8: Rheologies of slurries prepared with CFA-sodium silicate.

Rheology @ BHCT (rpm)	%CFA SS 0.25	0.5	0.75	1	1.5	2	2.5
300	31.5	43.5	24	37	31	44.5	40.5
200	24.5	38.5	19	33	25.5	40	36.5
100	19.5	36	18.5	26.5	24	37.5	33
60	17.5	32.5	19	26	23	36.5	31.5
30	15	31	17	27	21	36.5	31.5
6	8.5	17.5	14.5	15	16.5	22.5	22
3	10	8.5	12	11.5	10.5	19	17
P_v (cp)	18	11.25	8.25	15.75	10.5	10.5	11.25
Y_p (lb/100ft^2)	13.5	32.25	15.75	21.25	20.5	34	29.25

7.4 Strength development of the extended OWC slurries

Tables 8 and 9 show the compressive strength results for slurries containing com-Na_2SiO_3 and CFA-Na_2SiO_3 respectively. As expected, there was a decrease in compressive strength for all slurries as the

amount of water added increased. Figs 16, 17 and 18 show that the slurries containing CFA-Na_2SiO_3 had higher compressive strength than those containing com-Na_2SiO_3 at 8 hours, 12 hours and 24 hours respectively. From Tables 5 and 6 it can be observed that the CFA-Na_2SiO_3 slurries gained the compressive strength of 50 psi earlier than the Na_2SiO_3 slurries. This is the minimum strength required to hold the casing in position. The same observation was obtained for slurries which managed to gain compressive strength of 500 psi within the first 24 hours. 500 psi is the sufficient strength required to hold the casing where further drilling or perforation of the casing need to be done.

Table 9: UCA Results of slurries with commercial sodium silicate.

	% SS						
UCA Results	**0.25**	**0.5**	**0.75**	**1**	**1.5**	**2**	**2.5**
50psi (hrs: min)	2:12:00	2:09:00	3:22:30	2:12:00	2:49:00	3:11:30	3:40:00
500psi (hrs: min)	7:26:00	8:58:00	_	7:41:00	22:47:00	_	_
8hrs Compressive Strength(psi)	527	465	191	529	301	281	241
12hrs Compressive Strength(psi)	658	583	243	689	416	367	298
24hrs Compressive Strength(psi)	920	741	345	820	512	419	364

Table 10: UCA Results of slurries prepared with CFA-sodium silicate.

UCA Results	% CFA SS 0.25	0.5	0.75	1	1.5	2	2.5
50psi (hrs: min)	1:59:30	2:28:30	3:14:00	2:01:30	2:36:00	3:00:00	2:43:00
500psi(hrs:min)	5:41:00	8:45:30	_	7:37:30	21:43:30	_	_
8hrs Compressive Strength(psi)	643	471	236	601	319	307	253
12hrs Compressive Strength(psi)	842	597	321	714	439	381	351
24hrs Compressive Strength(psi)	1111	826	450	836	576	427	449

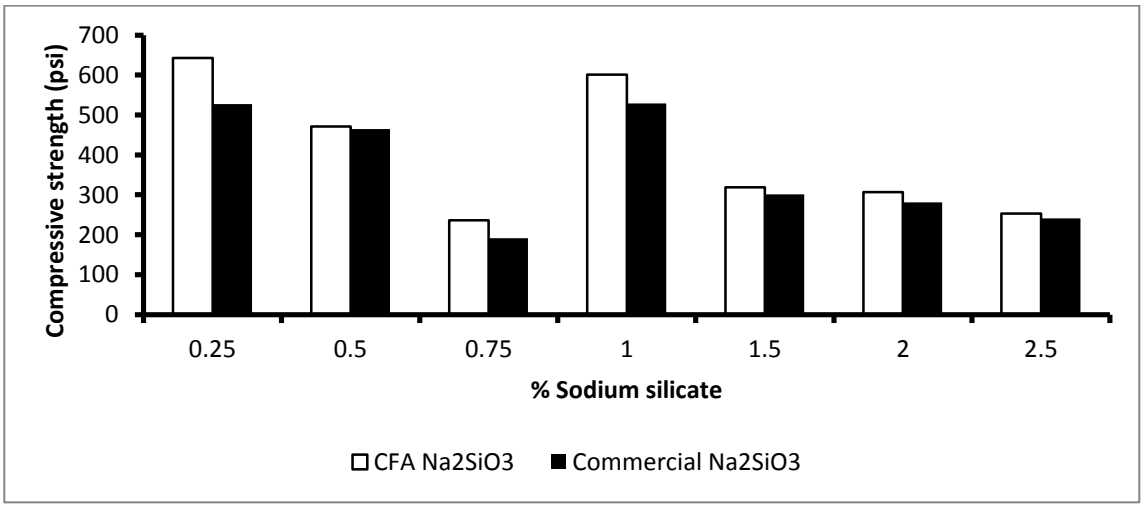

Figure 16: Compressive strength results at 8 hours.

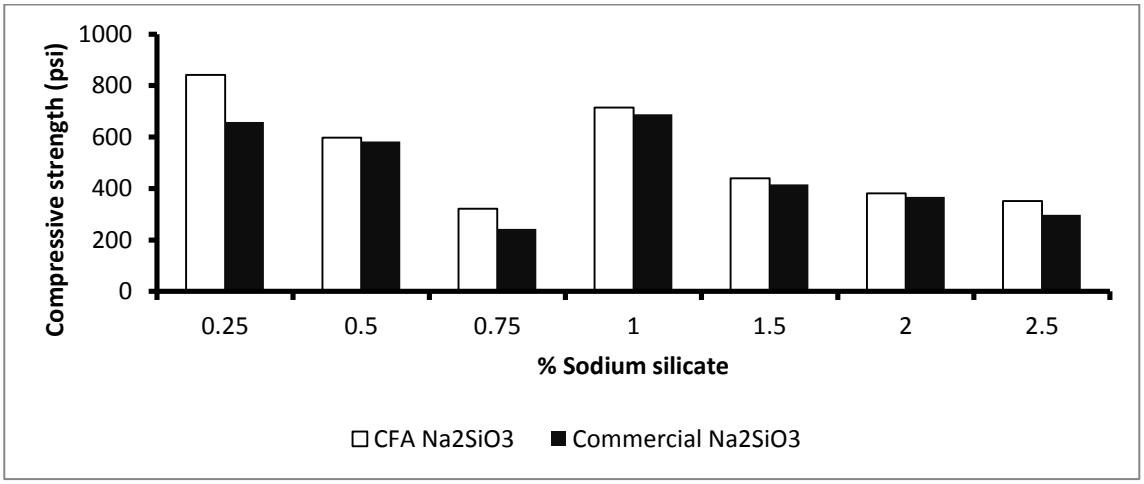

Figure 17: Compressive strength results at 12 hours

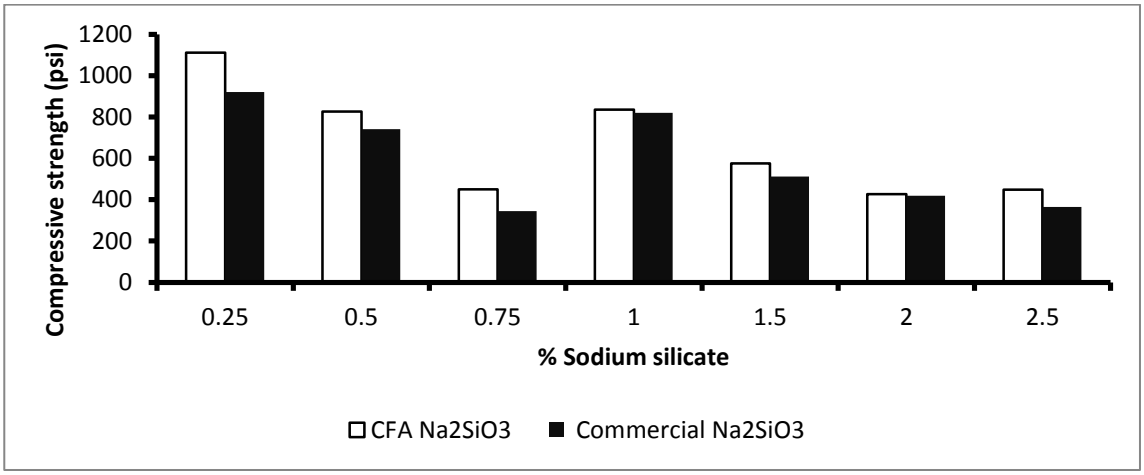

Figure 18: Compressive strength results at 24 hours.

7.5 Summary

As expected, there is a decrease in density and compressive strength as the amount of mix water increases. The results show that the synthesized CFA-Na_2SiO_3 was successfully used as an extender of OWC. All the slurries prepared managed to exceed the minimum TRRC compressive strength requirements for extender slurries (see Table 1). Furthermore, the slurries extended with CFA-Na_2SiO_3 are less viscous and have greater compressive strength compared to com-Na_2SiO_3 slurries. Evaluation of the thickening times of the slurries could not be done at the time when this study was carried out because the HPHT consistometer at the Baker Hughes South Africa was faulty, and at the time the report was submitted it has not been repaired. Since this study forms a part of a taught MSc degree programme in Petroleum Engineering (otherwise known as 50:50), the time allotted for research was too little for a comprehensive research. Consequently, thickening time analysis of the slurries could not be conducted. However, results from this study could be a platform upon which further research development in this area could be built. Hence, it is recommended that future studies should consider the analysis of thickening time of the slurries.

CHAPTER 8: GENERAL CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The aim of this study was to synthesize sodium silicate for use as an OWC extender, using mild temperature and pressure conditions and South African CFA as a SiO_2 source. The first part of this work involved the characterization of CFA. Results of this study indicate that the South African CFA used belongs to Class F of CFA and contains 58 % amorphous SiO_2 which was extracted at a yield of 41 %.

In the second part of the study, Na_2SiO_3 was synthesized using the extracted SiO_2 and NaOH. The physico-chemical properties of the synthesized Na_2SiO_3 are consistent with that of commercial Na_2SiO_3, indicating the purity of the as-prepared Na_2SiO_3 from the CFA. In addition, the synthesis protocol, which was at a mild temperature, confirms the energy efficiency of the method used.

The final part of the study involved the application of the synthesized Na_2SiO_3 as an OWC extender. Slurries extended with commercial Na_2SiO_3 were used as a standard for comparison. Results showed that all the slurries were in compliance with the TRRC Rule 13 requirements for development of compressive strength of extender slurries (see Table 1). The rheology results showed that CFA-Na_2SiO_3 makes slurries that are less viscous than com-Na_2SiO_3, which makes them less difficult to pump. Comparing the UCA results showed that the slurries extended with CFA-

Na_2SiO_3 have higher compressive strength than those containing com-Na_2SiO_3 (see Appendix A). This means that the WOC is reduced when CFA-Na_2SiO_3 is used as an additive and as a result the job can be completed in less time. Where early strength development is critical, CFA-Na_2SiO_3 slurries are therefore preferred.

8.2 Recommendations

There are some aspects concerning the synthesis process and the application of Na_2SiO_3 which were not within the scope of this study that require optimization or investigation. These include;

- Optimization of SiO_2 extraction from CFA. A study of methods or conditions for SiO_2 extraction with higher recoveries is recommended for the future.
- Evaluation of the thickening times of the slurries could not be done at the time when this study was carried out. This evaluation is therefore recommended for future studies.
- A study of the possibility of using CFA-Na_2SiO_3 in blocking gas migration in oil wells and also its possible use as a complement to a cement squeeze is also recommended.
- Evaluation of the performance of the CFA-Na_2SiO_3 as an additive to drilling fluid is also recommended for future studies.

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APPENDICES

Appendix A: UCA graphs of cement slurries.

These graphs present the development in compressive strength of the OWC slurries over time.

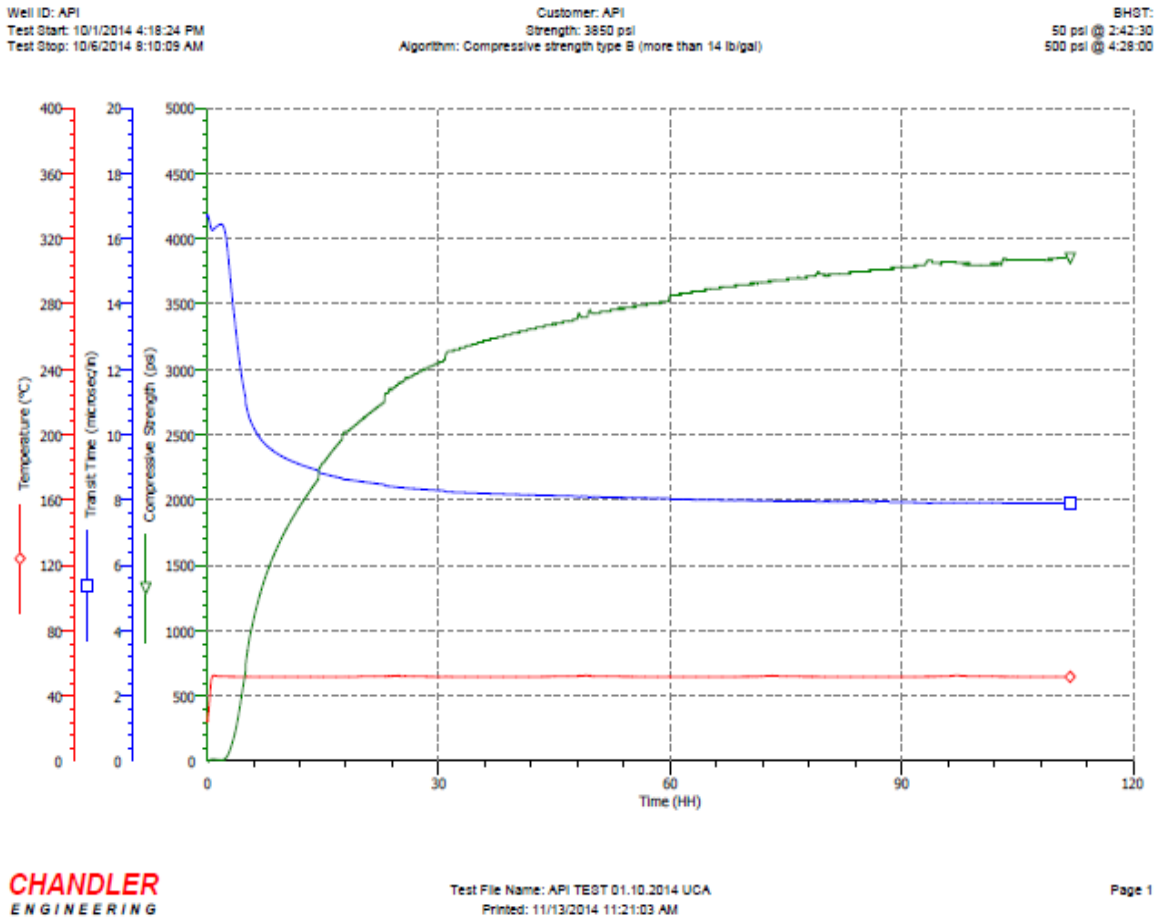

Fig A.1: Slurry containing 0 % additive

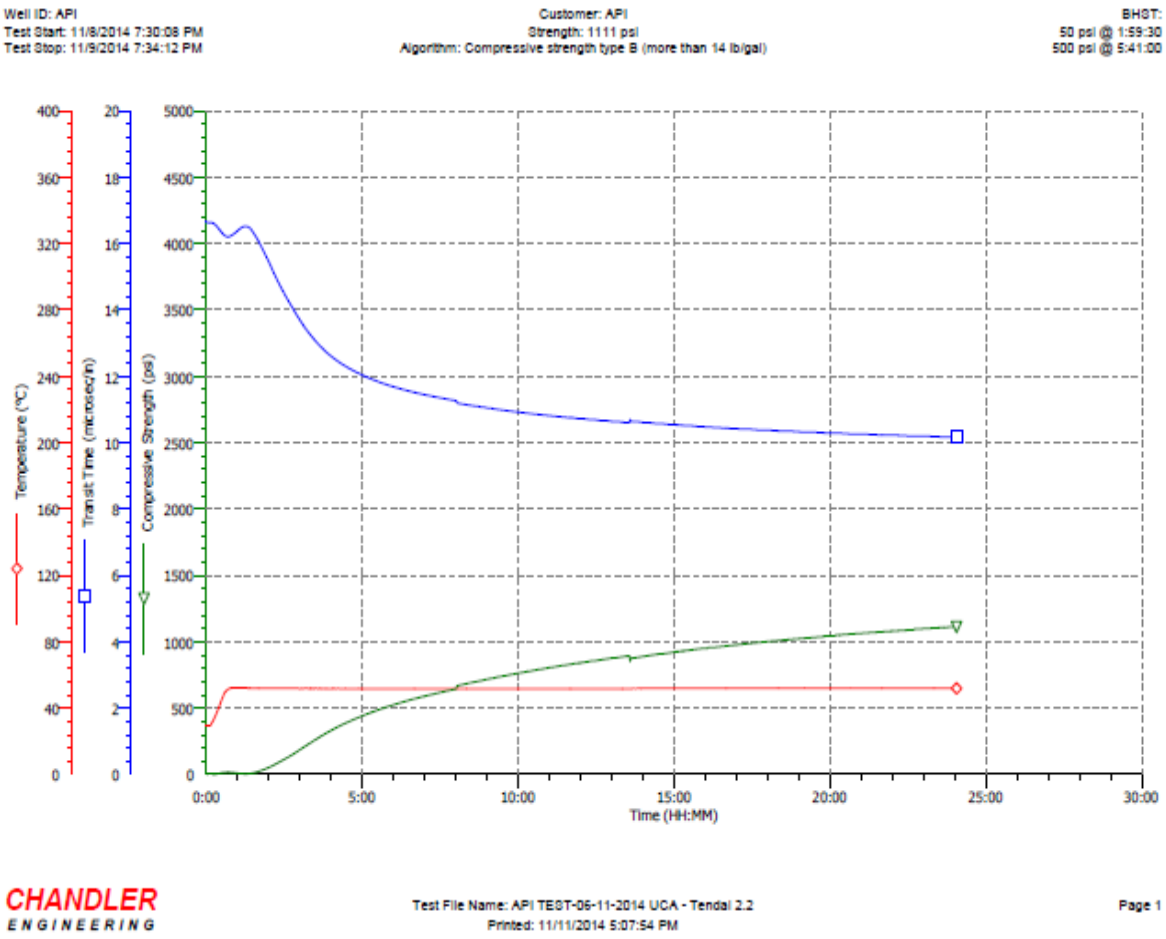

Fig A.2: Slurry containing 0.25 % CFA-Na_2SiO_3

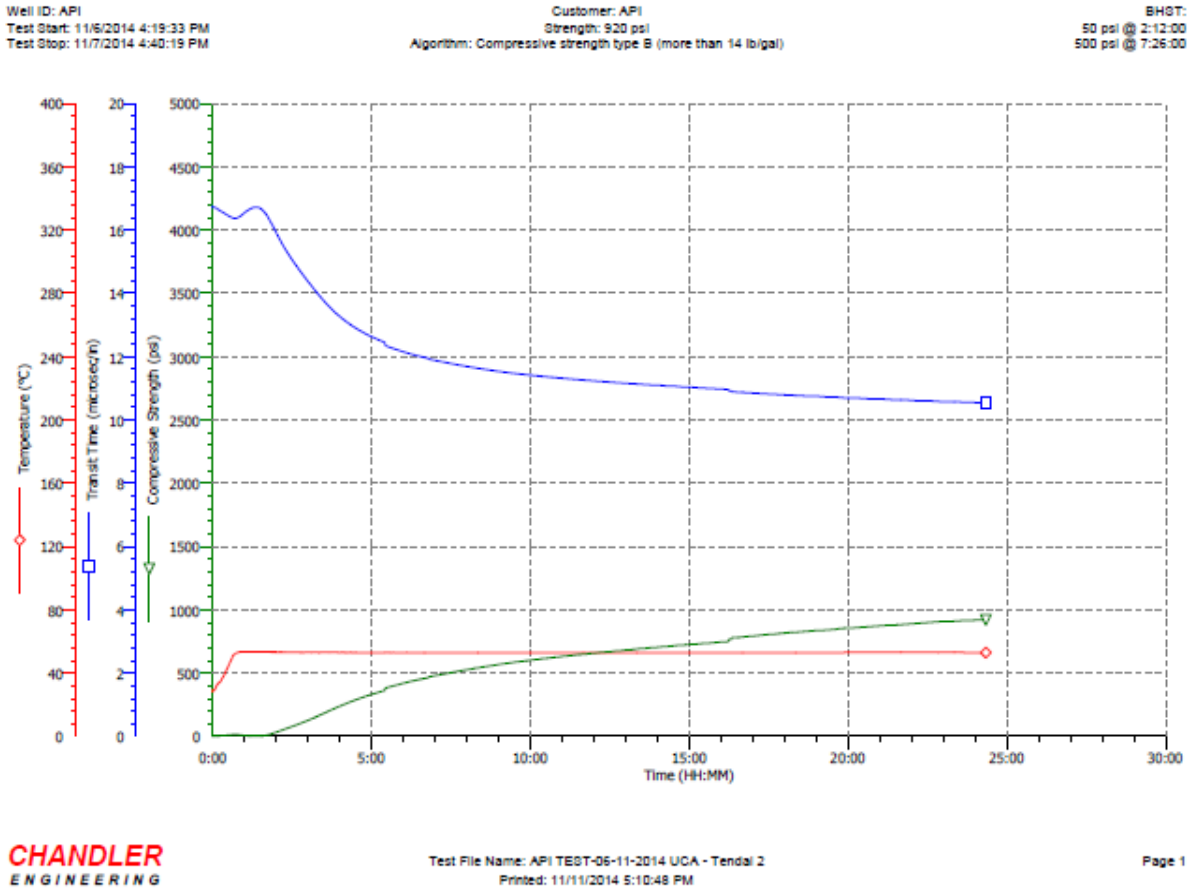

Fig A.3: Slurry containing 0.25 % com-Na_2SiO_3

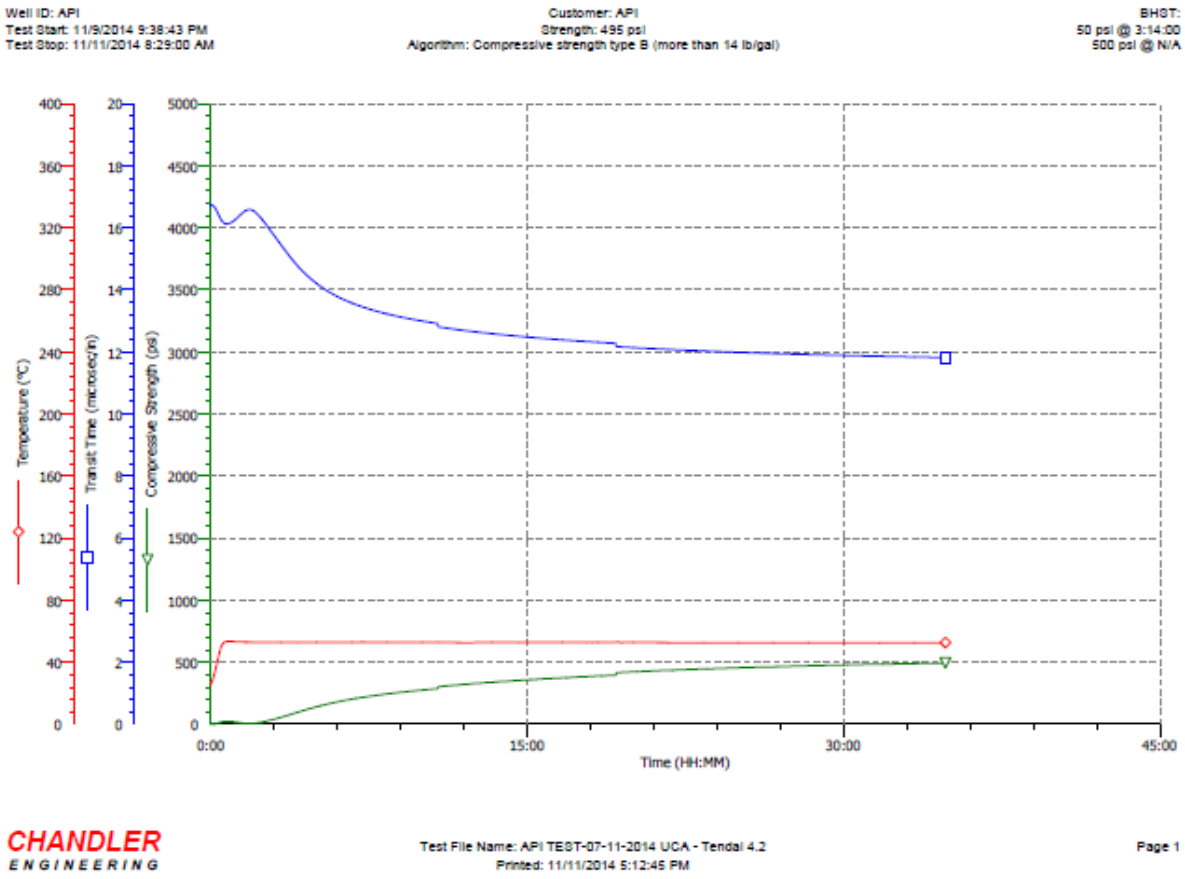

Fig A.4: Slurry containing 0.75 % CFA-Na_2SiO_3

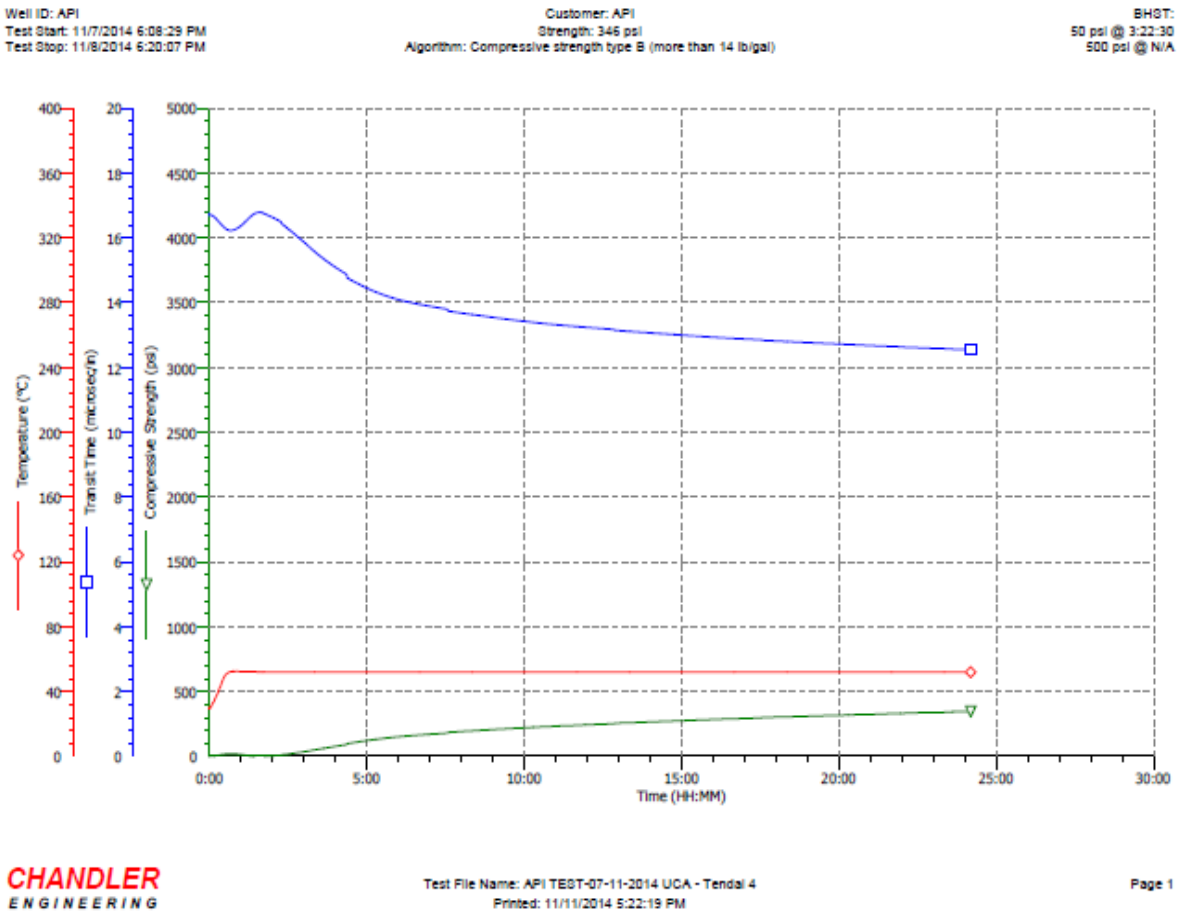

Fig A.5: Slurry containing 0.75 % com-Na_2SiO_3

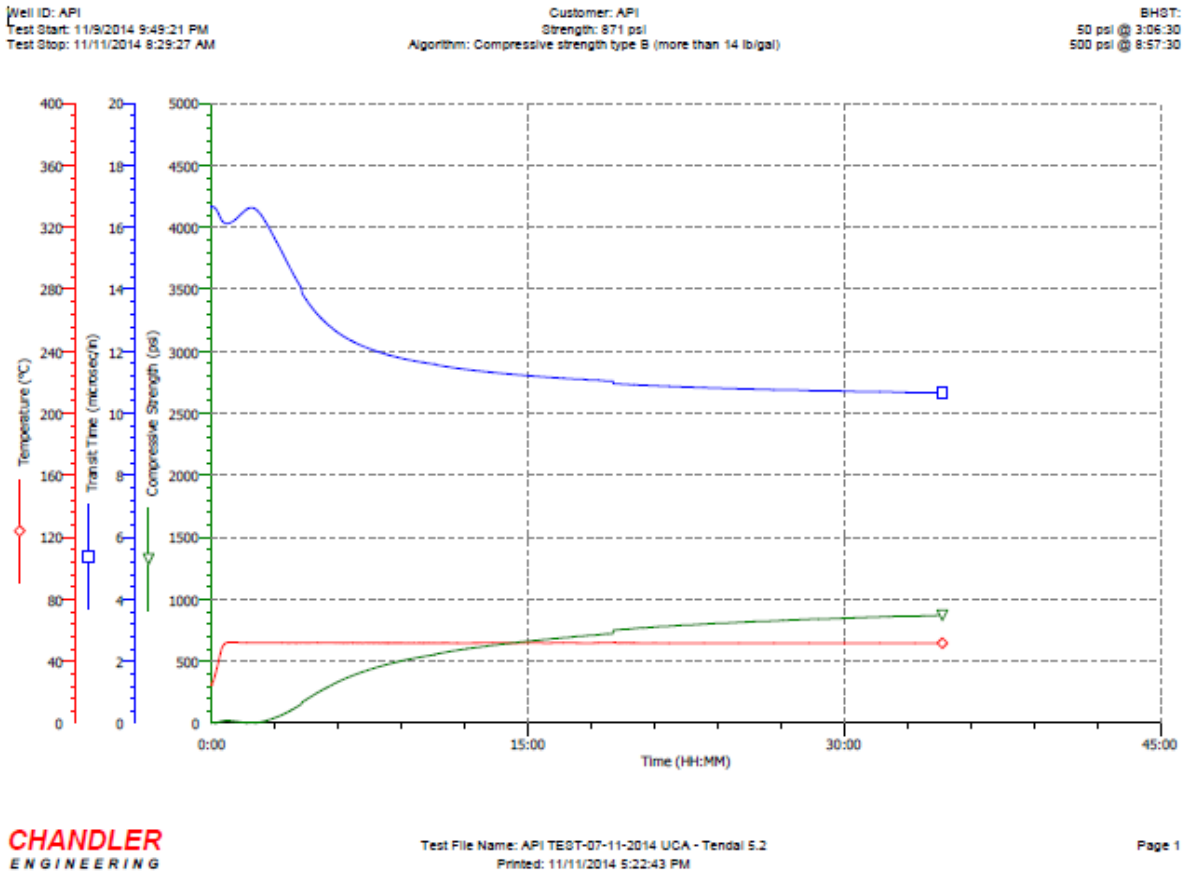

Fig A.6: Slurry containing 1 % CFA-Na_2SiO_3

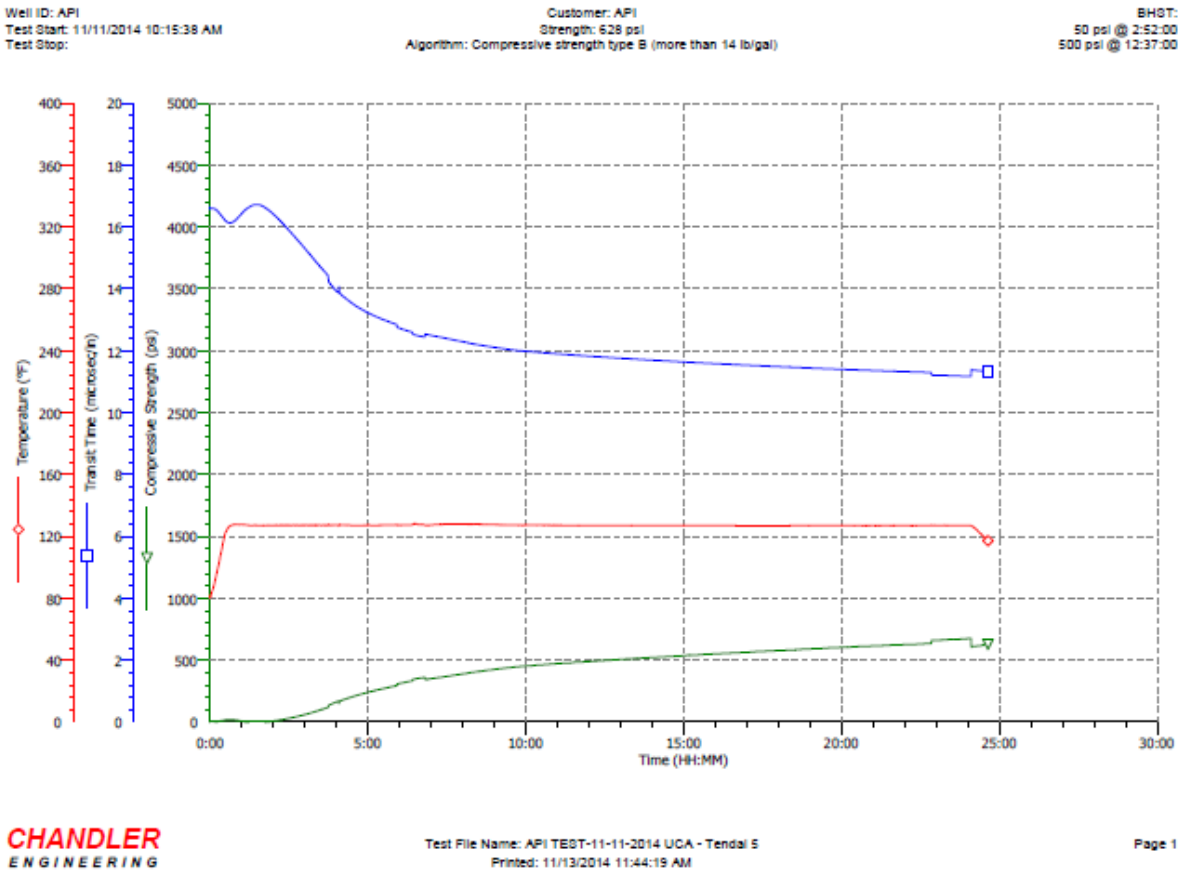

Fig A.7: Slurry containing 1 % com-Na_2SiO_3

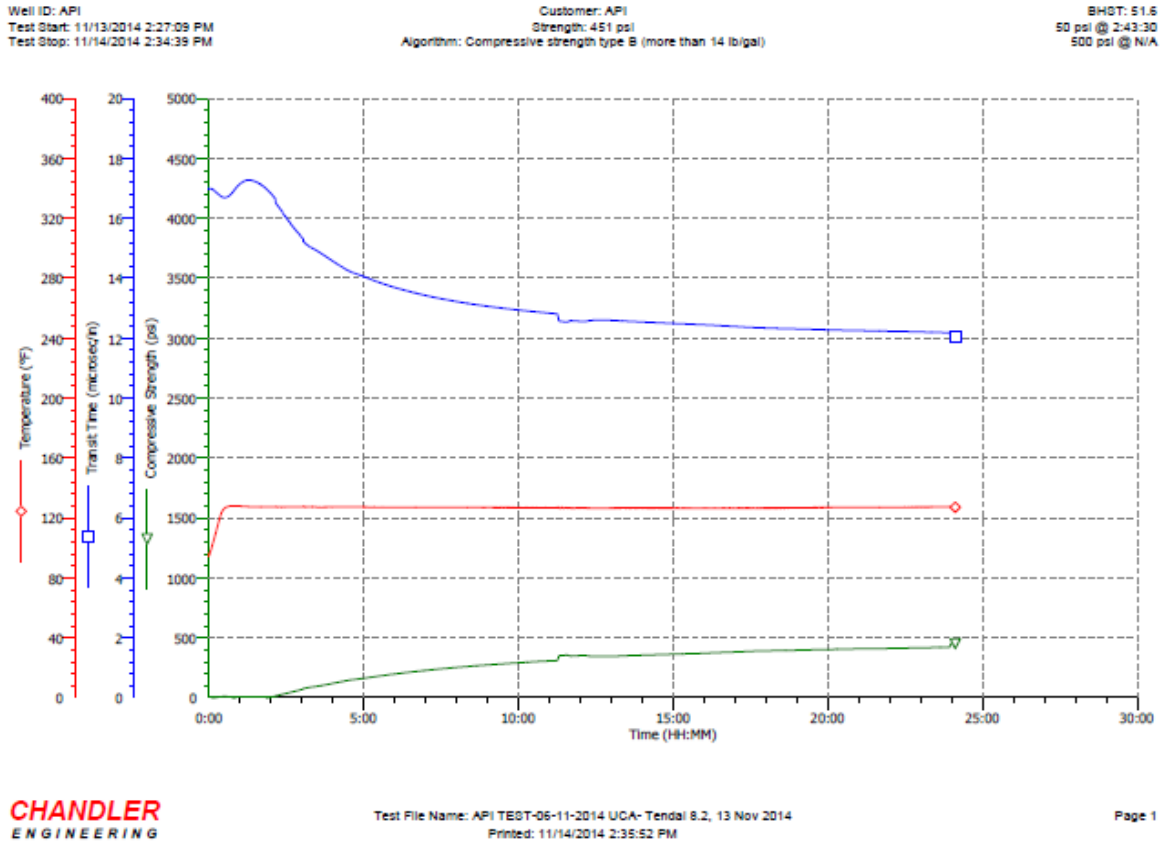

Fig A.8: Slurry containing 2.5 % CFA-Na_2SiO_3

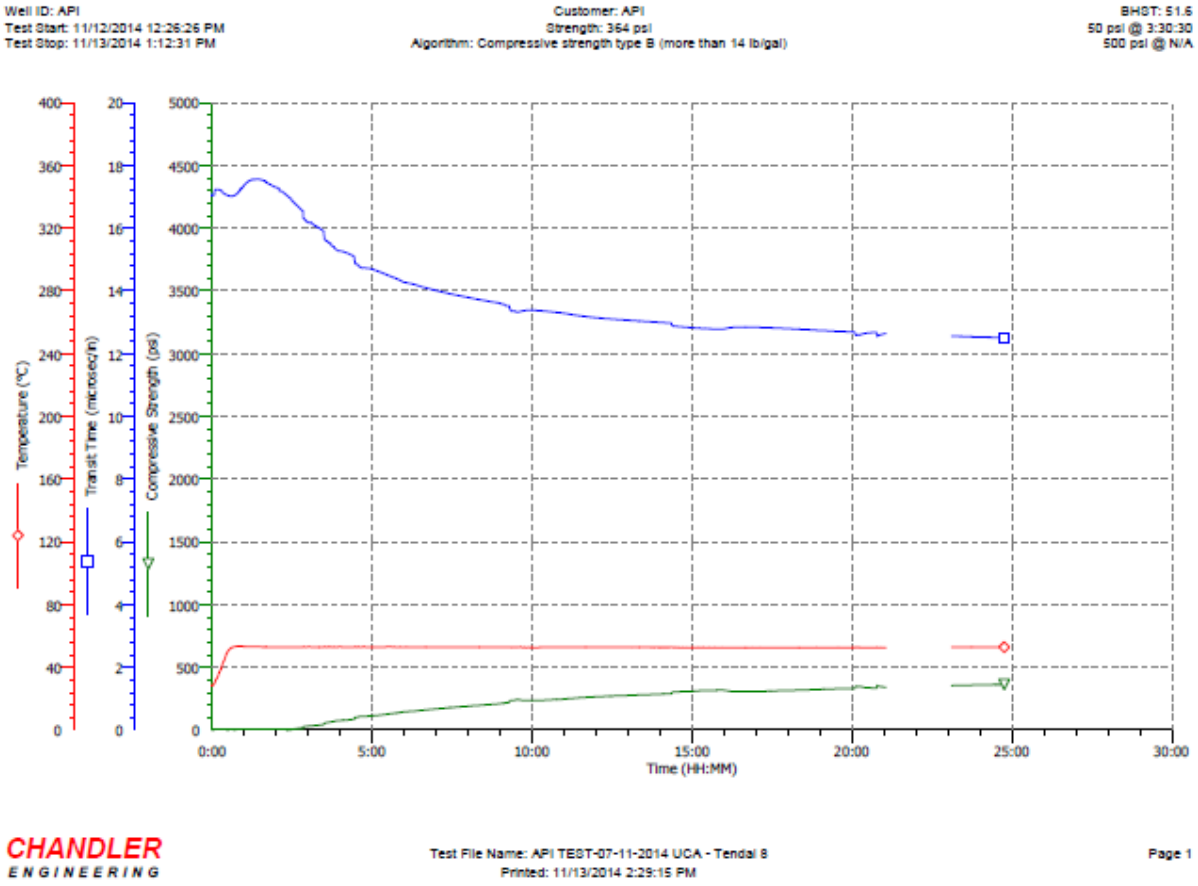

Fig A.9: Slurry containing 2.5 % com-Na_2SiO_3

Appendix B: Manuscript under review

This is a copy of the manuscript which was submitted to the Southern African Institute of Mining and Metallurgy Journal and is currently under review.

Appendix C: Conference Paper

This is a copy of the paper which was presented at the 1st International Conference on Oilfield Chemistry & Flow Assurance. Oilflow 2015. June 22 – 24, 2015. Port Harcourt, Rivers State, Nigeria.