During the oil and gas well cementing process, some wells often lose circulation zones, and they are therefore prone to formation breakage. Often, low-density slurries are required to overcome these problems, and extenders, which help to reduce the weight of the slurry, are utilized (Salim and Amani 2013; Ahmaruzzaman 2010; Shahriar 2011). The commonly used extenders are water extenders such as bentonite and sodium silicate, which allow addition of water to the slurry; and low-density aggregates such as microspheres and pozzolans, which have densities lower than that of Portland cement (3.15 g.cm\(^{-3}\)) (Nelson et al., 1990). These extenders reduce the density of the slurry, resulting in a reduction of the hydrostatic pressure during cementing (Nelson et al., 1990). Extenders also increase slurry yield by replacing a substantial amount of the cement required to complete a given task, thereby reducing the expenditure.

One of the most commonly used water extenders for oil well cement (OWC) is sodium silicate (Na\(_2\)SiO\(_3\)). It has been reported that Na\(_2\)SiO\(_3\) as a water extender is five times more effective than bentonite (Nelson et al. 1990). Unlike pozzolanic extenders such as fly ash, Na\(_2\)SiO\(_3\) is highly reactive with OWC (Joel and Ujile, 2009). Na\(_2\)SiO\(_3\) 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, hence the accelerating effect of Na\(_2\)SiO\(_3\) (Joel and Ujile, 2009). A low concentration of Na\(_2\)SiO\(_3\) is required for a high yield as compared to other extenders such as bentonite and raw coal fly ash, making it a preferred additive for OWC (Joel and Ujile 2009). While fly ash is added in concentrations of up to 50% by weight of cement (BWOC) and bentonite up to 20% BWOC, Na\(_2\)SiO\(_3\) additions range from 0.2% to 3.0% BWOC (Nelson et al., 1990). The accelerating effect of Na\(_2\)SiO\(_3\), however, limits its application at lower temperatures, typically at less than 52°C bottom hole circulating temperature (BHCT) (Nelson et al., 1990; Joel and Ujile 2009). However, it can be used at higher temperatures with the addition of a retarder, although in the presence of a retarder, the effectiveness of Na\(_2\)SiO\(_3\) as an extender is reduced because of the inhibition of C-S-H formation (Nelson et al., 1990; Joel and Ujile, 2009).

Synthesis of sodium silicate from South African coal fly ash and its use as an extender in oil well cement applications

by T. Kaduku*, M.O. Daramola*, F.O. Obazu*, and S.E. Iyuke*

Synopsis
In this work, the use of sodium silicate derived from South African coal fly ash (CFA) in oil well cement (OWC) applications is reported. Silica (SiO\(_2\)) was extracted from the CFA and used to synthesize CFA-derived sodium silicate (CFA-Na\(_2\)SiO\(_3\)), a typical OWC slurry extender. The physico-chemical properties of the CFA-Na\(_2\)SiO\(_3\) were compared to those of a commercial sodium silicate (com-Na\(_2\)SiO\(_3\)) using scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy. OWC slurries with varying proportions of cement, distilled water, and 2% CaCl\(_2\) by weight of water (BWOW) were prepared and extended using the CFA-Na\(_2\)SiO\(_3\) and the com-Na\(_2\)SiO\(_3\) at compositions ranging from 0.25-2.5% by weight of cement (BWOC). Rheological properties of the slurries were evaluated using American Petroleum Institute procedures and compared. The physico-chemical properties of the CFA-Na\(_2\)SiO\(_3\) are consistent with those of com-Na\(_2\)SiO\(_3\), indicating the purity of the CFA-Na\(_2\)SiO\(_3\). A comparative study of the OWC slurries indicated that the slurries extended with CFA-Na\(_2\)SiO\(_3\) have slightly lower densities, lower viscosities, and higher compressive strength than those extended with com-Na\(_2\)SiO\(_3\). This indicates that CFA-Na\(_2\)SiO\(_3\) slurries would be easier to pump and preferable where early strength development is critical. This report could be instrumental in providing a way for the beneficiation of South African CFA in the petroleum, oil, and gas industry.

Keywords
oil well cementing, coal fly ash, sodium silicate, compressive strength.

Introduction
During the oil and gas well cementing process, some wells often lose circulation zones, and they are therefore prone to formation breakage. Often, low-density slurries are required to overcome these problems, and extenders, which help to reduce the weight of the slurry, are utilized (Salim and Amani 2013; Ahmaruzzaman 2010; Shahriar 2011). The commonly used extenders are water extenders such as bentonite and sodium silicate, which allow addition of water to the slurry; and low-density aggregates such as microspheres and pozzolans, which have densities lower than that of Portland cement (3.15 g.cm\(^{-3}\)) (Nelson et al., 1990). These extenders reduce the density of the slurry, resulting in a reduction of the hydrostatic pressure during cementing (Nelson et al., 1990). Extenders also increase slurry yield by replacing a substantial amount of the cement required to complete a given task, thereby reducing the expenditure.
Synthesis of sodium silicate from South African coal fly ash

At industrial scale, commercial sodium silicate is traditionally manufactured by calcination of sodium carbonate (Na2CO3) and SiO2 at a temperature range 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 to air pollution. Alternatively, Na2SiO3 can be produced by the reaction of SiO2 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 Na2SiO3 for use as an additive to OWC. In addition, the SiO2, one of the raw materials required in the aforementioned alternative preparation method of Na2SiO3, can be obtained from coal fly ash (CFA).

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; 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). The use of CFA in OWC has been reported (Shahrriar, 2011), but composition of the CFA differs from country to country and this could affect its suitability as additive in OWC operations. Furthermore, the use of raw CFA results in slower strength gain and longer setting times, contributing to air pollution. Alternatively, Na2SiO3 can be obtained by the reaction of SiO2 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 Na2SiO3 for use as an additive to OWC. In addition, the SiO2, one of the raw materials required in the aforementioned alternative preparation method of Na2SiO3, can be obtained from coal fly ash (CFA).

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Materials and methods

Materials

Class G cement was obtained from Dyckerhoff, Germany, and CFA from a power station in South Africa. Demineralized water was prepared in-house. Hydrochloric acid solution (37%), sodium hydroxide pellets (98% purity), calcium chloride (99.99% purity), and commercial sodium metasilicate (95%) were purchased from Sigma Aldrich and used as delivered without any modification or purification.

Methods

CFA sample preparation and characterization

Small quantities of CFA were scooped randomly from different points and then mixed together to make the representative sample. The CFA samples were characterized using X-ray diffraction (XRD: Brucker D2 X-ray diffraction machine), X-ray fluorescence (XRF: PANalytical AXIOS X-ray fluorescence spectrometer), scanning electron microscopy (SEM: Zeiss Sigma VP field emission scanning electron microscope), and thermogravimetric analysis (TGA: TGA DSC STA 600 with Pyris software). The pH of CFA (slurried in water) was measured using a Metrohm 744 pH meter, and the particle size distribution of the CFA was obtained using a Malvern Mastersizer 2000.

Extraction of SiO2 and preparation of Na2SiO3 from CFA

The metal oxides such as Al2O3 and CaO were removed from CFA by acid refluxing using 3 M HCl at 100°C for 6 hours as described by Tang et al. (2012). The solid product, SiO2, was filtered out and purified by successive washings with demineralized water. The wet SiO2 was dried in an oven at 200°C for 2 hours to obtain an amorphous silica powder which was then analysed using SEM-EDX, XRD, and Fourier transform infrared spectroscopy (FTIR: Bruker Tensor 27 Fourier transform infrared spectrometer). 60 g of the amorphous silica was reacted with 80 g sodium hydroxide pellets in 100 ml distilled water in a Pyrex flat-bottomed flask at 80°C and atmospheric pressure to produce a colourless viscous solution. The solution was then poured into a crucible and calcined at 300°C for 3 hours to produce a white solid (CFA-Na2SiO3) which was crushed to a powder using a mortar and pestle. The product was then subjected to SEM-EDX, XRD, and FTIR analyses.

Preparation and characterization of cement slurries

Slurries containing varying amounts of cement, distilled water, 2% calcium chloride (CaCl2) by weight of water (BWOW), com-Na2SiO3, and CFA-Na2SiO3 were prepared and their densities, rheology, and thickening times evaluated. A Chandler Ametek constant speed mixer (Model 50-60) was used for mixing and the slurries were pre-conditioned using a Chandler Ametek Atmospheric Consistometer (Model 1200) prior to the rheology tests. The rheology tests were conducted using a Chandler Ametek automated viscometer (Model 5550) and a Chandler Ametek pressurized mud balance was used to determine the density of the slurries. A Chandler Ametek twin cell ultrasonic cement analyser (UCA) (Model 4262) was used to determine the development of compressive strength of the slurries. All the tests on the cement slurries were carried out according to the specification for materials and testing for well cements (American Petroleum Institute Specification 10A, 2002). The compositions of the slurries are presented in Table I.

Results and discussion

CFA sample preparation and characterization

Figure 1 shows the XRD patterns for the CFA. The patterns are consistent with those reported for previously studied South African CFAs (Ayanda et al., 2012; Mainganye et al., 2013; Ikotun et al., 2014). Table II shows the XRF analysis of the CFA together with results from reports in the literature (Ayanda et al., 2012; Mainganye et al., 2013). The major components of the CFA are silica, alumina, iron oxide, calcium oxide, and carbon (inferred from the loss on ignition (LOI) test). The CFA is of class F (ASTM C618, 2012). The metal oxide contents decreased in the order SiO2 > Al2O3 > Fe2O3 > CaO > MgO > K2O > Na2O > TiO2. This is consistent with previous reports on South African CFA (Ayanda et al., 2012; Mainganye et al., 2013; Ikotun et al., 2014). Interestingly,
the CFA contained about 58% SiO2, which is one of the required materials for the synthesis of Na2SiO3.

The morphology of the CFA is depicted in the SEM micrograph in Figure 2. The shapes of the CFA particles are determined by the exposure conditions (time and temperature) in the combustion chamber (Fisher et al., 1978). As seen in Figure 2, most of the particles are spherical, especially in the finer fractions. A similar observation has been reported for other South African CFAs (Ayanda et al., 2012; 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, while 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 (<1 μm) 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 arise mainly from incomplete combustion of coal components (Fisher et al., 1978). Furthermore, the TGA shows that the CFA contains about 0.2% moisture, 1.6% volatile matter, and 1.7% fixed carbon. The particle size ranges from 0.32–112 μm. These results are also in agreement with previous studies (Ayanda et al., 2012; 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. This could be attributed to the dissolution of compounds such as CaO in the CFA. This observation is in good agreement with previous reports (Ayanda et al., 2012).

Synthesis of sodium silicate from South African coal fly ash

| Table 1 | Compositions and densities of the slurries |
|---|---|---|---|
| Sodium silicate (% BWOC) | Water (%) | Class G cement (g) | Slurry density (lb/gal) |
| | | | (com-Na2SiO3) | (CFA-Na2SiO3) |
| 0 | 44 | 792 | 15.8 | 15.8 |
| 0.25 | 66 | 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 |

Extraction of SiO2, preparation and characterization of Na2SiO3 from CFA

The morphologies of the extracted SiO2, synthesized CFA-Na2SiO3, and com-Na2SiO3 were characterized by SEM. Figure 3 shows the SEM images of the extracted SiO2. Similar images for precipitated SiO2 have been reported in the literature (Music et al., 2011). The elemental compositions obtained using energy dispersive X-ray spectroscopy (EDS) (not shown in this manuscript) indicated the presence of Si and O, confirming the presence of SiO2. The XRD pattern in Figure 4 shows the characteristic slope and pattern for amorphous SiO2, consisting of a broad band with a peak which indicates that the substance is amorphous and contains pure SiO2 (Saikia et al., 2008; Essien et al., 2011; Music et al., 2011; Okoronwo et al., 2013). Similar patterns for amorphous silica have been recorded in the literature (Saikia et al., 2008; Okoronwo et al., 2013). The two sharp peaks in the pattern are due to the presence of quartz, corroborating the results obtained from EDS. The FTIR spectrum of the SiO2 is depicted in Figure 5. The bands of absorption at 1199 cm–1, 964 cm–1, and 682 cm–1 can be attributed to the absorption peaks characteristic of SiO2 (Ying-Mei et al., 2010). The absorption peak at 1199 cm–1

Figure 1 – XRD diffractogram for two samples of CFA

Figure 2 – SEM micrograph of the South African CFA
Synthesis of sodium silicate from South African coal fly ash

corresponds to the asymmetrical stretching vibration of Si–O (Ying-Mei et al., 2010). In addition, the 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).

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The XRD patterns for CFA-Na₂SiO₃ and com-Na₂SiO₃ are shown in Figure 6. The two patterns are similar, although a small 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-Na₂SiO₃. The shift in the peaks could be attributed to the small quantity of the sample used in the analysis. Figure 7 depicts the SEM images for CFA-Na₂SiO₃ and com-Na₂SiO₃. The morphology of the CFA-Na₂SiO₃ is totally different from that of com-Na₂SiO₃. However, the EDS results showed the same elemental components with different compositions. Figure 8 shows the FTIR spectra for the com-Na₂SiO₃ and CFA-Na₂SiO₃. The FTIR analysis of the two samples indicates that there is no observable chemical difference between the samples. 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 sodium metasilicate (Miller and Wilkins, 1952). The stretch between 1500 cm⁻¹ and 2000 cm⁻¹ could be attributed to the presence of Si–OH and bending vibration absorption of the O–H bond (Ying-Mei et al., 2010).

The compositions and the densities of the slurries prepared using CFA-Na₂SiO₃ and com-Na₂SiO₃ as additives are shown in Table I. The slurries had similar densities, with slight differences as the amount of additive added increased. Some of the slurries containing CFA-Na₂SiO₃ had slightly lower densities compared to the slurries containing com-Na₂SiO₃. There was a 0.02% difference in the densities of the slurries containing 2% additive (CFA-Na₂SiO₃ and com-Na₂SiO₃). The difference may be due to the fact that slurries prepared using CFA-Na₂SiO₃ contained a lot of froth. The rheologies of slurries prepared using CFA-Na₂SiO₃ and com-Na₂SiO₃ as additives are shown in Tables III and IV, respectively. The

Preparation and characterization of cement slurries

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slurries prepared using both additives exhibited good rheology, with plastic viscosities (Pv) between 3.75 and 18.75 cp and yield points (Yp) between 13.5 and 61.75 lb/100 ft². The slurries containing com-Na₂SiO₃ generally had higher rheological values than those prepared using the CFA-Na₂SiO₃. At 60 r/min the viscosity of the slurry containing 1% com-Na₂SiO₃ was 45 cp, while that for the CFA-Na₂SiO₃ slurry was 26 cp. The slurries prepared using CFA-Na₂SiO₃ were less viscous and this can be attributed to the presence of froth.

It is known that the use of sodium silicate as a water extender in OWC operation helps to prevent breakdown of weak formations and loss of circulation (Nelson et al., 1990). In addition, it helps to lower the hydrostatic pressure, thereby enhances the ‘pumpability’ of the cement slurry (Nelson et al., 1990). When sodium silicate is used as a water extender in OWC operation, it reacts with calcium hydroxide in the cement slurry to produce a viscous C-S-H gel that allows addition of large volume of water to the slurry, thereby

| Element | Power station CFA | Composition, % |
|---------|------------------|----------------|
|         |                  | Mainganye et al., 2013 | Ayanda et al., 2012 |
| SiO₂    | 57.9             | 55.66          | 51.43          |
| Al₂O₃   | 31.12            | 27.95          | 30.33          |
| Fe₂O₃   | 0.33             | 3.22           | 2.29           |
| FeO     | 2.65             | NR             | NR             |
| MnO     | 0.04             | 0.04           | 0.02           |
| MgO     | 0.55             | 1.91           | 1.95           |
| CaO     | 4.28             | 4.38           | 4.75           |
| Na₂O    | 0.13             | 0.31           | 0.54           |
| K₂O     | 0.66             | 0.48           | 0.77           |
| TiO₂    | 1.519            | 1.13           | 1.74           |
| P₂O₅    | 0.39             | 0.26           | 1.08           |
| Cr₂O₃   | 0.0223           | 0.03           | 0.02           |
| NO      | 0.0008           | NR             | 0.01           |
| LOI     | 0.73             | 4.74           | 1.21           |
| Sum     | 100.72           | 100.07         | 99.28          |
Synthesis of sodium silicate from South African coal fly ash

### Table III

**Rheological properties of the slurries with com-\(\text{Na}_2\text{SiO}_3\)**

| Rheology @ BHCT (r/min) | 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  | 33| 33  |
| 3                       | 12   | 12  | 11.5 | 20| 25  | 27| 29.5|
| \(P_r\) (cp)            | 7.5  | 14.25| 3.75 | 18.75| 18| 12| 8.25|
| \(Y_p\) (lb/100 ft²)    | 21.5 | 28.25| 17.75| 40.25| 58| 52| 61.75|

### Table IV

**Rheological properties of the slurries with CFA-\(\text{Na}_2\text{SiO}_3\)**

| Rheology @ BHCT (r/min) | 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| 15  | 22.5| 22  |
| 3                       | 10   | 8.5 | 12   | 11.5| 10.5| 19 | 17  |
| \(P_r\) (cp)            | 18   | 11.25| 8.25 | 15.75| 10.5| 10.5| 11.25|
| \(Y_p\) (lb/100 ft²)    | 13.5 | 32.25| 15.75| 21.25| 20.5| 34 | 29.25|

### Table V

**UCA results for the slurries with com-\(\text{Na}_2\text{SiO}_3\)**

| % SS | 0.25 | 0.5 | 0.75 | 1 | 1.5 | 2 | 2.5 |
|------|------|-----|------|---|-----|---|-----|
| 0.34 MPa (h: min) | 2:12:00 | 2:09:00 | 3:22:30 | 2:12:00 | 2:49:00 | 3:11:30 | 3:40:00 |
| 3.4 MPa (h: min) | 7:26:00 | 8:58:00 | 7:41:00 | 22:47:00 |
| 8 h compressive strength (MPa) | 3.64 | 3.21 | 1.32 | 3.65 | 2.08 | 1.94 | 1.66 |
| 12 h compressive strength (MPa) | 4.54 | 4.02 | 1.68 | 4.75 | 2.87 | 2.53 | 2.06 |
| 24 h compressive strength (MPa) | 6.35 | 5.11 | 2.38 | 5.66 | 3.53 | 2.89 | 2.51 |

### Table VI

**UCA results for the slurries with CFA-\(\text{Na}_2\text{SiO}_3\)**

| % CFA SS | 0.25 | 0.5 | 0.75 | 1 | 1.5 | 2 | 2.5 |
|----------|------|-----|------|---|-----|---|-----|
| 0.34 MPa (h: min) | 1:59:30 | 2:28:30 | 3:14:00 | 2:01:30 | 2:36:00 | 3:00:00 | 2:43:00 |
| 3.4 MPa (h: min) | 5:41:00 | 8:45:30 | 7:37:30 | 21:43:30 |
| 8 h compressive strength (MPa) | 4.44 | 3.25 | 1.83 | 4.15 | 2.20 | 2.12 | 1.75 |
| 12 h compressive strength (MPa) | 5.81 | 4.12 | 2.21 | 4.93 | 3.03 | 2.63 | 2.42 |
| 24 h compressive strength (MPa) | 7.67 | 5.70 | 3.11 | 5.77 | 3.97 | 2.95 | 3.10 |
reducing the density of the slurry and increasing its yield. From the results from the rheology analysis of the CFA-Na$_2$SiO$_3$ prepared from CFA in this study and tested in the formulation of OWC slurries, it is obvious that slurries prepared with CFA-Na$_2$SiO$_3$ might be preferable to those prepared with com-Na$_2$SiO$_3$ for an OWC operation that requires early strength development.

Tables V and VI show the compressive strength results for slurries containing com-Na$_2$SiO$_3$ and CFA-Na$_2$SiO$_3$, respectively. As expected, there was a decrease in compressive strength for all slurries as the amount of water added increased. This is consistent with findings from the literature. An increase in water-to-cement ratio results in a dramatic decrease in the compressive strength of the slurries (Fawzi, 2012), Figures 9–11 show that the slurries containing CFA-Na$_2$SiO$_3$ had higher compressive strength than those containing com-Na$_2$SiO$_3$ at 8 hours, 12 hours and 24 hours. From Tables V and VI, it can be observed that the CFA-Na$_2$SiO$_3$ slurries gained a compressive strength of 0.34 MPa earlier than the Na$_2$SiO$_3$ slurries. This is the minimum strength required to hold the casing in position. In addition, the earlier gain of the compressive strength by the slurries with CFA-Na$_2$SiO$_3$ indicates that the slurries with CFA-Na$_2$SiO$_3$ set quicker than those with com-Na$_2$SiO$_3$. The results obtained from the ultrasonic cement analyser (UCA) also indicate that the same observation was obtained for slurries that attained a compressive strength of 5.4 MPa within the first 24 hours. A strength of 5.4 MPa is sufficient to hold the casing when further drilling or perforation of the casing is required.

Conclusions
The results indicate that the South African CFA used in this study is a Class F CFA and contains 58% amorphous SiO$_2$. The physico-chemical properties of the synthesized Na$_2$SiO$_3$ are consistent with those of the commercial Na$_2$SiO$_3$, indicating the purity of the as-prepared Na$_2$SiO$_3$ from the CFA. In addition, the synthesis protocol, which was at a mild temperature, confirms the energy efficiency of the method used. Cement slurries prepared with CFA-Na$_2$SiO$_3$ show better performance than those prepared with com-Na$_2$SiO$_3$. Rheological testing indicated that the slurries prepared with CFA-Na$_2$SiO$_3$ are less viscous than those prepared with com-Na$_2$SiO$_3$. The CFA-Na$_2$SiO$_3$ slurries will thus be easier to pump and handle during OWC operation compared to the slurries prepared with com-Na$_2$SiO$_3$. UCA analysis showed that the slurries prepared with CFA-Na$_2$SiO$_3$ have higher compressive strength in comparison to those prepared from the com-Na$_2$SiO$_3$. Although a small concentration of sodium silicate (0.2% to 3.0% BWOC) is always used in OWC operations to yield a reasonable compressive strength (Nelson et al., 1990), the higher compressive strength of the slurries with CFA-Na$_2$SiO$_3$ implies that smaller amounts of CFA-Na$_2$SiO$_3$ will be required for OWC operations. In addition, slurries prepared with CFA-Na$_2$SiO$_3$ will be preferable to those prepared with com-Na$_2$SiO$_3$ for an OWC operation that requires early strength development. The results of this study could provide a platform for further research development on the beneficiation of South African CFA in the petroleum, oil, and gas industry.

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Synthesis of sodium silicate from South African coal fly ash

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