



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

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## 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 ( $\text{SiO}_2$ ) was extracted from the CFA and used to synthesize CFA-derived sodium silicate ( $\text{CFA-Na}_2\text{SiO}_3$ ), a typical OWC slurry extender. The physico-chemical properties of the  $\text{CFA-Na}_2\text{SiO}_3$  were compared to those of a commercial sodium silicate ( $\text{com-Na}_2\text{SiO}_3$ ) 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%  $\text{CaCl}_2$  by weight of water (BWOW) were prepared and extended using the  $\text{CFA-Na}_2\text{SiO}_3$  and the  $\text{com-Na}_2\text{SiO}_3$  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  $\text{CFA-Na}_2\text{SiO}_3$  are consistent with those of  $\text{com-Na}_2\text{SiO}_3$ , indicating the purity of the  $\text{CFA-Na}_2\text{SiO}_3$ . A comparative study of the OWC slurries indicated that the slurries extended with  $\text{CFA-Na}_2\text{SiO}_3$  have slightly lower densities, lower viscosities, and higher compressive strength than those extended with  $\text{com-Na}_2\text{SiO}_3$ . This indicates that  $\text{CFA-Na}_2\text{SiO}_3$  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 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 ( $3.15 \text{ g.cm}^{-3}$ ) (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 ( $\text{Na}_2\text{SiO}_3$ ). It has been reported that  $\text{Na}_2\text{SiO}_3$  as a water extender is five times more effective than bentonite (Nelson *et al.* 1990). Unlike pozzolanic extenders such as fly ash,  $\text{Na}_2\text{SiO}_3$  is highly reactive with OWC (Joel and Ujile, 2009).  $\text{Na}_2\text{SiO}_3$  reacts with the  $\text{Ca}^{2+}$  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  $\text{Na}_2\text{SiO}_3$  (Joel and Ujile, 2009). A low concentration of  $\text{Na}_2\text{SiO}_3$  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,  $\text{Na}_2\text{SiO}_3$  additions range from 0.2% to 3.0% BWOC (Nelson *et al.*, 1990). The accelerating effect of  $\text{Na}_2\text{SiO}_3$ , however, limits its application at lower temperatures, typically at less than  $52^\circ\text{C}$  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  $\text{Na}_2\text{SiO}_3$  as an extender is reduced because of the inhibition of C-S-H formation (Nelson *et al.*, 1990; Joel and Ujile, 2009).

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At industrial scale, commercial sodium silicate is traditionally manufactured by calcination of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and  $\text{SiO}_2$  at a temperature range of 1400–1500°C in furnaces (Folletto *et al.*, 2006). Although the raw materials are cheap, the process is not cost-effective due to its high energy consumption and maintenance cost (Folletto *et al.*, 2006). The process also emits dust, nitrogen, and sulphur oxides, contributing to air pollution. Alternatively,  $\text{Na}_2\text{SiO}_3$  can be produced by the reaction of  $\text{SiO}_2$  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  $\text{Na}_2\text{SiO}_3$  for use as an additive to OWC. In addition, the  $\text{SiO}_2$ , one of the raw materials required in the aforementioned alternative preparation method of  $\text{Na}_2\text{SiO}_3$ , 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; Folletto *et al.*, 2006; Okoronkwo *et al.*, 2013). The use of CFA in OWC has been reported (Shahriar, 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, thereby resulting in low early-age strength and delays in the well completion process (Bazzar *et al.*, 2013). In South Africa, about 25 Mt of CFA is produced annually and its disposal constitutes a huge environmental problem. In this study,  $\text{SiO}_2$  was extracted from CFA and used as starting material to synthesize  $\text{Na}_2\text{SiO}_3$ . The potential use of the synthesized CFA-derived sodium silicate as an OWC extender was evaluated and compared with that of commercial sodium silicate (com-  $\text{Na}_2\text{SiO}_3$ ).

## 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: Bruker 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 $\text{SiO}_2$ and preparation of $\text{Na}_2\text{SiO}_3$ from CFA

The metal oxides such as  $\text{Al}_2\text{O}_3$  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,  $\text{SiO}_2$ , was filtered out and purified by successive washings with demineralized water. The wet  $\text{SiO}_2$  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- $\text{Na}_2\text{SiO}_3$ ) 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 ( $\text{CaCl}_2$ ) by weight of water (BWOW), com- $\text{Na}_2\text{SiO}_3$ , and CFA- $\text{Na}_2\text{SiO}_3$  were prepared and their densities, rheology, and thickening times evaluated. A Chandler Ametek constant speed mixer (Model 30-60) 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 3530) 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  $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{CaO} > \text{MgO} > \text{K}_2\text{O} > \text{Na}_2\text{O} > \text{TiO}_2$ . This is consistent with previous reports on South African CFA (Ayanda *et al.*, 2012; Mainganye *et al.*, 2013; Ikotun *et al.*, 2014). Interestingly,

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Table 1

Compositions and densities of the slurries

Sodium silicate (% BWOc)	Water (%)	Class G cement (g)	Slurry density (lb/gal) (com-Na <sub>2</sub> SiO <sub>3</sub> )	Slurry density (lb/gal) (CFA-Na <sub>2</sub> SiO <sub>3</sub> )
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

the CFA contained about 58% SiO<sub>2</sub>, which is one of the required materials for the synthesis of Na<sub>2</sub>SiO<sub>3</sub>.

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).

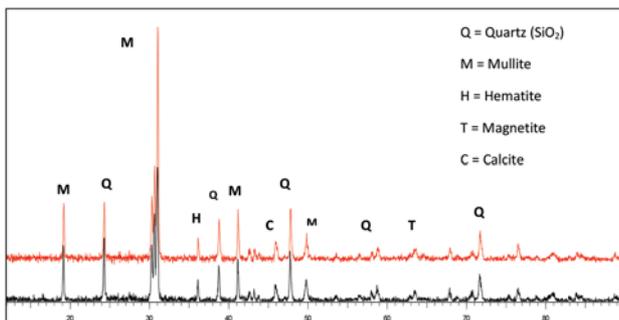


Figure 1 – XRD diffractogram for two samples of CFA

## Extraction of SiO<sub>2</sub>, preparation and characterization of Na<sub>2</sub>SiO<sub>3</sub> from CFA

The morphologies of the extracted SiO<sub>2</sub>, synthesized CFA-Na<sub>2</sub>SiO<sub>3</sub>, and com-Na<sub>2</sub>SiO<sub>3</sub> were characterized by SEM. Figure 3 shows the SEM images of the extracted SiO<sub>2</sub>. Similar images for precipitated SiO<sub>2</sub> 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 SiO<sub>2</sub>. The XRD pattern in Figure 4 shows the characteristic slope and pattern for amorphous SiO<sub>2</sub>, consisting of a broad band with a peak which indicates that the substance is amorphous and contains pure SiO<sub>2</sub> (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 SiO<sub>2</sub> is depicted in Figure 5. The bands of absorption at 1199 cm<sup>-1</sup>, 964 cm<sup>-1</sup>, and 682 cm<sup>-1</sup> can be attributed to the absorption peaks characteristic of SiO<sub>2</sub> (Ying-Mei *et al.*, 2010). The absorption peak at 1199 cm<sup>-1</sup>

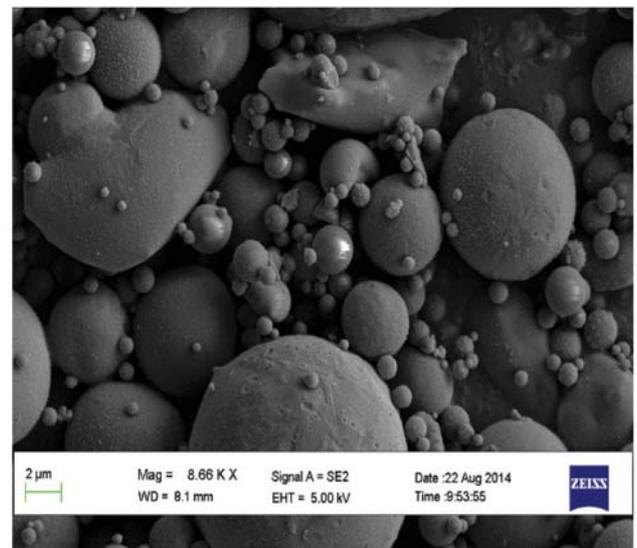


Figure 2 – SEM micrograph of the South African CFA

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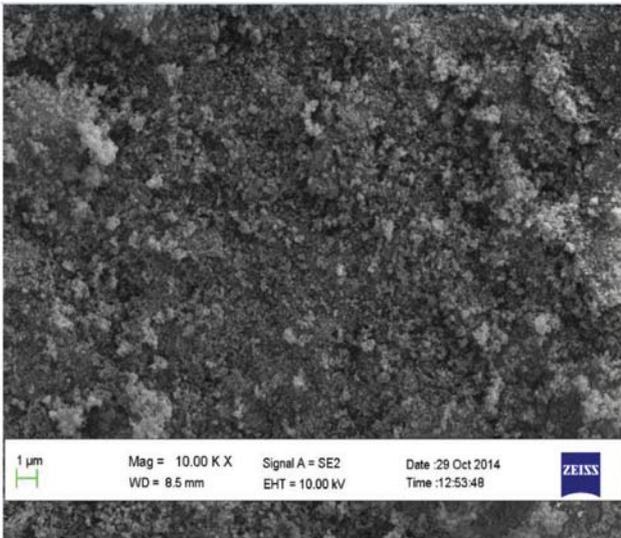


Figure 3 – SEM micrograph of amorphous silica extracted from the South African CFA

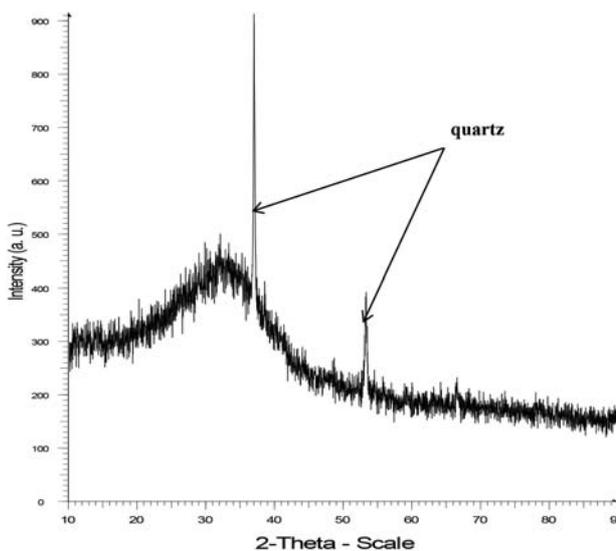


Figure 4 – XRD spectra of the amorphous silica extracted from the South Africa CFA

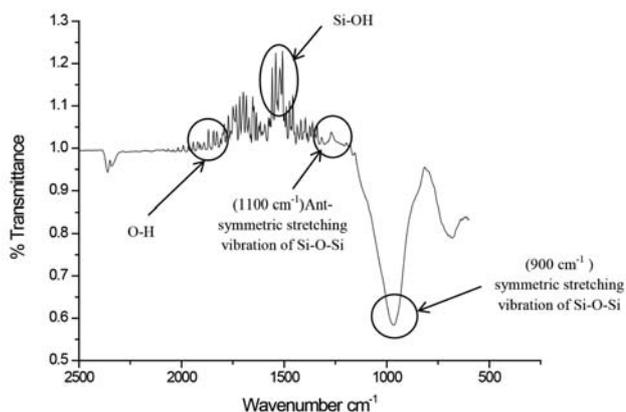


Figure 5 – FTIR spectra of the amorphous silica extracted from the South African CFA

corresponds to the asymmetrical stretching vibration of Si–O (Ying-Mei *et al.*, 2010). In addition, the absorption peaks at  $964\text{ cm}^{-1}$  and  $682\text{ cm}^{-1}$  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  $1500\text{ cm}^{-1}$  and  $2000\text{ cm}^{-1}$  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).

The XRD patterns for CFA- $\text{Na}_2\text{SiO}_3$  and com- $\text{Na}_2\text{SiO}_3$  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- $\text{Na}_2\text{SiO}_3$ . 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- $\text{Na}_2\text{SiO}_3$  and com- $\text{Na}_2\text{SiO}_3$ . The morphology of the CFA- $\text{Na}_2\text{SiO}_3$  is totally different from that of com- $\text{Na}_2\text{SiO}_3$ . However, the EDS results showed the same elemental components with different compositions. Figure 8 shows the FTIR spectra for the com- $\text{Na}_2\text{SiO}_3$  and CFA- $\text{Na}_2\text{SiO}_3$ . The FTIR analysis of the two samples indicates that there is no observable chemical difference between the samples. Both samples show absorption bands at  $2340\text{ cm}^{-1}$ ,  $1160\text{ cm}^{-1}$ ,  $1125\text{ cm}^{-1}$ ,  $980\text{ cm}^{-1}$ , and  $715\text{ cm}^{-1}$  that characterize the presence of sodium metasilicate (Miller and Wilkins, 1952). The stretch between  $1500\text{ cm}^{-1}$  and  $2000\text{ cm}^{-1}$  could be attributed to the presence of Si–OH and bending vibration absorption of the O–H bond (Ying-Mei *et al.*, 2010).

### Preparation and characterization of cement slurries

The compositions and the densities of the slurries prepared using CFA- $\text{Na}_2\text{SiO}_3$  and com- $\text{Na}_2\text{SiO}_3$  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- $\text{Na}_2\text{SiO}_3$  had slightly lower densities compared to the slurries containing com- $\text{Na}_2\text{SiO}_3$ . There was a 0.02% difference in the densities of the slurries containing 2% additive (CFA- $\text{Na}_2\text{SiO}_3$  and com- $\text{Na}_2\text{SiO}_3$ ). The difference may be due to the fact that slurries prepared using CFA- $\text{Na}_2\text{SiO}_3$  contained a lot of froth. The rheologies of slurries prepared using CFA- $\text{Na}_2\text{SiO}_3$  and com- $\text{Na}_2\text{SiO}_3$  as additives are shown in Tables III and IV, respectively. The

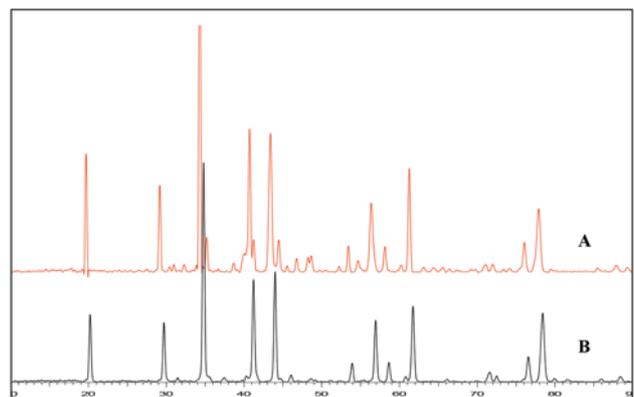


Figure 6 – XRD diffractograms of commercial sodium silicate (B: com- $\text{Na}_2\text{SiO}_3$ ) and CFA sodium silicate (A: CFA- $\text{Na}_2\text{SiO}_3$ )

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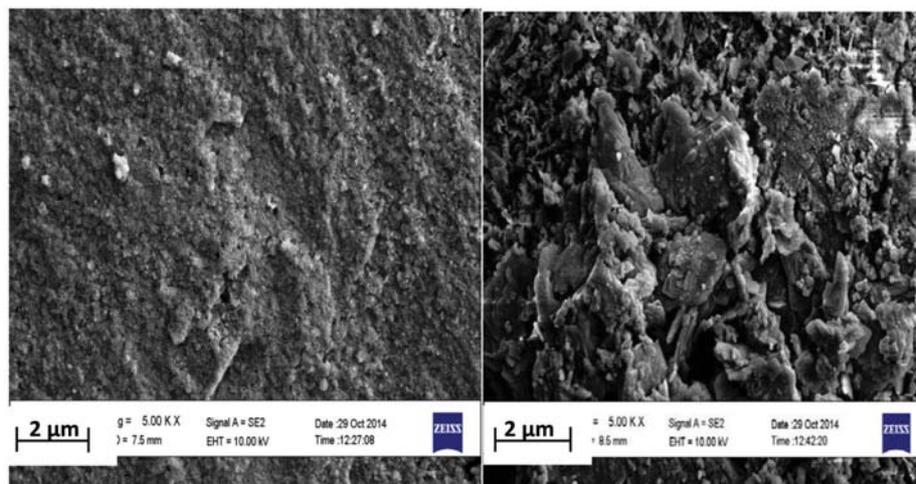


Figure 7 – SEM micrographs of com- $\text{Na}_2\text{SiO}_3$  (left) and CFA- $\text{Na}_2\text{SiO}_3$  (right)

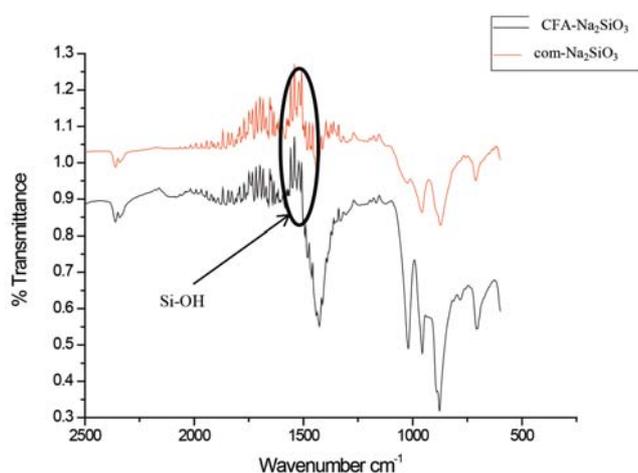


Figure 8 – FTIR spectra of commercial sodium silicate (com- $\text{Na}_2\text{SiO}_3$ ) and CFA sodium silicate (CFA- $\text{Na}_2\text{SiO}_3$ )

slurries prepared using both additives exhibited good rheology, with plastic viscosities ( $P_v$ ) between 3.75 and 18.75 cp and yield points ( $Y_p$ ) between 13.5 and 61.75 lb/100 ft<sup>2</sup>. The slurries containing com- $\text{Na}_2\text{SiO}_3$  generally had higher rheological values than those prepared using the CFA- $\text{Na}_2\text{SiO}_3$ . At 60 r/min the viscosity of the slurry containing 1% com- $\text{Na}_2\text{SiO}_3$  was 45 cp, while that for the CFA- $\text{Na}_2\text{SiO}_3$  slurry was 26 cp. The slurries prepared using CFA- $\text{Na}_2\text{SiO}_3$  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

Table II

XRF results for the power station CFA (majors), compared with other South African CFAs (Mainganye *et al.*, 2013; Ayanda *et al.*, 2012)

Element	Power station CFA	Composition, %	
		Mainganye <i>et al.</i> , 2013	Ayanda <i>et al.</i> , 2012
SiO <sub>2</sub>	57.9	55.66	51.43
Al <sub>2</sub> O <sub>3</sub>	31.12	27.95	30.93
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	0.13	0.31	0.54
K <sub>2</sub> O	0.66	0.48	0.77
TiO <sub>2</sub>	1.519	1.13	1.74
P <sub>2</sub> O <sub>5</sub>	0.39	0.26	1.08
Cr <sub>2</sub> O <sub>3</sub>	0.0223	0.03	0.02
NiO	0.0008	NR	0.01
LOI	0.73	4.74	1.21
<b>Sum</b>	<b>100.72</b>	<b>100.07</b>	<b>99.28</b>

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Table III

### Rheological properties of the slurries with com- $\text{Na}_2\text{SiO}_3$

Rheology @ BHCT (r/min)	com- $\text{Na}_2\text{SiO}_3$ , %						
	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/100 ft <sup>2</sup> )	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)	CFA- $\text{Na}_2\text{SiO}_3$ , %						
	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/100 ft <sup>2</sup> )	13.5	32.25	15.75	21.25	20.5	34	29.25

Table V

### UCA results for the slurries with com- $\text{Na}_2\text{SiO}_3$

UCA results	% 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- $\text{Na}_2\text{SiO}_3$

UCA results	% 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	1.63	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
24h compressive strength (MPa)	7.67	5.70	3.11	5.77	3.97	2.95	3.10

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reducing the density of the slurry and increasing its yield. From the results from the rheology analysis of the CFA- $\text{Na}_2\text{SiO}_3$  prepared from CFA in this study and tested in the formulation of OWC slurries, it is obvious that slurries prepared with CFA- $\text{Na}_2\text{SiO}_3$  might be preferable to those prepared with com- $\text{Na}_2\text{SiO}_3$  for an OWC operation that requires early strength development.

Tables V and VI show the compressive strength results for slurries containing com- $\text{Na}_2\text{SiO}_3$  and CFA- $\text{Na}_2\text{SiO}_3$ , 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- $\text{Na}_2\text{SiO}_3$  had higher compressive strength than those containing com- $\text{Na}_2\text{SiO}_3$  at 8 hours, 12 hours and 24 hours. From Tables V and VI, it can be observed that the CFA- $\text{Na}_2\text{SiO}_3$  slurries gained a compressive strength of 0.34 MPa earlier than the  $\text{Na}_2\text{SiO}_3$  slurries. This is the minimum strength required to hold the casing in position. In addition, the earlier gain of the compressive strength by the with CFA- $\text{Na}_2\text{SiO}_3$  slurries indicates that the slurries with CFA- $\text{Na}_2\text{SiO}_3$  set quicker than those with com- $\text{Na}_2\text{SiO}_3$ . The results obtained from the ultrasonic cement analyser (UCA)

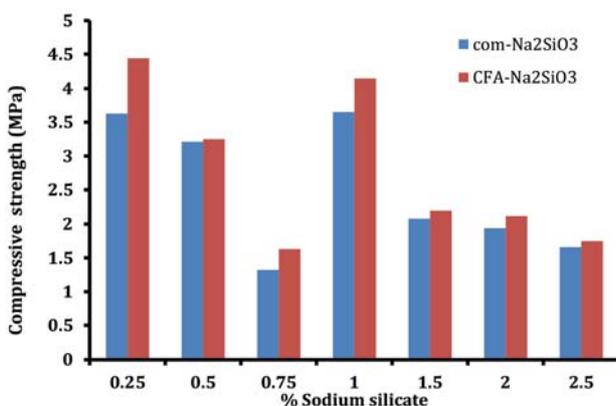


Figure 9 – Compressive strength results at 8 hours

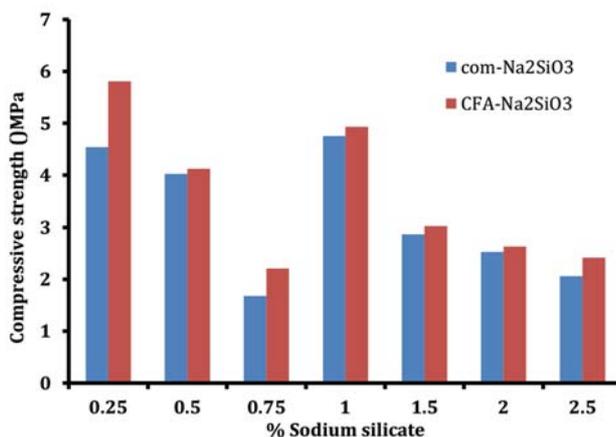


Figure 10 – Compressive strength results at 12 hours

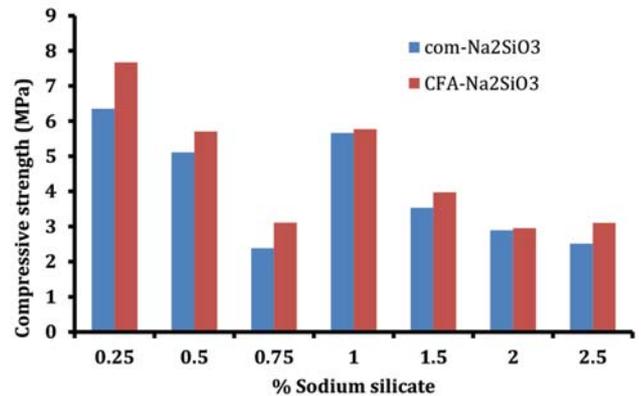


Figure 11 – Compressive strength results at 24 hours

also indicate that the same observation was obtained for slurries that attained a compressive strength of 3.4 MPa within the first 24 hours. A strength of 3.4 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  $\text{SiO}_2$ . The physico-chemical properties of the synthesized  $\text{Na}_2\text{SiO}_3$  are consistent with those of the commercial  $\text{Na}_2\text{SiO}_3$ , indicating the purity of the as-prepared  $\text{Na}_2\text{SiO}_3$  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- $\text{Na}_2\text{SiO}_3$  show better performance than those prepared with com- $\text{Na}_2\text{SiO}_3$ . Rheological testing indicated that the slurries prepared with CFA- $\text{Na}_2\text{SiO}_3$  are less viscous than those prepared with com- $\text{Na}_2\text{SiO}_3$ . The CFA- $\text{Na}_2\text{SiO}_3$  slurries will thus be easier to pump and handle during OWC operation compared to the slurries prepared with com- $\text{Na}_2\text{SiO}_3$ . UCA analysis showed that the slurries prepared with CFA- $\text{Na}_2\text{SiO}_3$  have higher compressive strength in comparison to those prepared from the com- $\text{Na}_2\text{SiO}_3$ . 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- $\text{Na}_2\text{SiO}_3$  implies that smaller amounts of CFA- $\text{Na}_2\text{SiO}_3$  will be required for OWC operations. In addition, slurries prepared with CFA- $\text{Na}_2\text{SiO}_3$  will be preferable to those prepared with com- $\text{Na}_2\text{SiO}_3$  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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