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Beneficiation of South African Coal-fly Ash in Oil Well Cement Operation

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Abstract

About 25 million tons of coal fly ash (CFA) is produced annually in South Africa. In this work, beneficiation of South African CFA in Oil Well Cementing (OWC) operation is reported. Silica (SiO_2) was extracted from the CFA and used to synthesize sodium silicate (CFA-Na_2SiO_3), typical OWC slurry extender. Physicochemical properties of the CFA-Na_2SiO_3 were compared to those of a commercial sodium silicate (com-Na_2SiO_3) using SEM, XRD, and FTIR. OWC slurries with varying compositions of cement, distilled water, and 2 % $CaCl_2$ by-weight-of-water (BWOW) were prepared and extended using the CFA-Na_2SiO_3 and the com-Na_2SiO_3 at compositions ranging from 0.25-2.5 % by-weight-of-cement (BWOC). Rheological properties of the slurries were evaluated using API procedures and compared. The physicochemical properties of the CFA-Na_2SiO_3 are consistent with that of com-Na_2SiO_3, indicating the purity of the CFA-Na_2SiO_3. A comparative study between the OWC slurries indicates 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. This report opens up a way for the beneficiation of South African CFA in the petroleum, oil and gas industry.

Keywords: Beneficiation; Oil well cement; Coal fly ash; Sodium silicate; Compressive strength; Oil and Gas.

1. Introduction

South Africa is mainly dependent on coal-fired power stations for electricity production, and about 25 million tons of coal fly ash (CFA) is produced annually. Disposal of this waste constitutes a huge environmental problem at the moment. Although the use of CFA in oil well cement (OWC) has been reported [1], but the composition of the CFA differs from country to country, and this could affect its suitability as an additive in OWC operation. In addition, 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 [2]. Against this background, this work reports for the first time in open literature, the beneficiation of South African CFA in OWC operation.

During the oil and gas well cementing process, 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 which help to reduce the weight of the slurry are utilized [1,3-4]. The commonly used extenders are water extenders such as bentonite and sodium silicate, which allow the 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}) [5]. These extenders reduce the density of the slurry, resulting in a reduction of the hydrostatic pressure during cementing [5]. 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, which is s reported to be about five times more effective as an extender compared to bentonite [5]. Na_2SiO_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 that provides sufficient viscosity to allow the use of large quantities of mix water without excessive free water separation [5]. The further C-S-H formation also results in a reduction in thickening time, and hence the accelerating effect of Na_2SiO_3 [6]. Traditionally, sodium silicate is manufactured in commercial quantity through high-temperature calcination (at 1400-1500°C) of sodium carbonate (Na_2CO_3) and SiO_2 in furnaces, making the process highly energy intensive translating to high operational cost [7]. In addition, waste effluents (dust, nitrogen and sulphur oxides) from the process contribute to air pollution.

As a way of overcoming the aforementioned shortcoming, manufacture of Na_2SiO_3 through a reaction between SiO_2 and NaOH at high temperature and pressure in an autoclave has been reported [8]. Although the method is still energy intensive, but the pollutants emitted are not potentially harmful to the environment. In light of the information at hand, it is essential to investigate an energy-efficient method for producing Na_2SiO_3 for use as an additive in cementing operation, most importantly from waste material. Against this background, this work investigated the possibility of synthesizing Na_2SiO_3 from South African CFA and evaluating the performance of the synthesized Na_2SiO_3 in cementing operation.

2. Material and methods

2.1. Materials

Class G cement (from Dyckerhoff), CFA (from Power Station-X in South Africa), demineralized water (prepared in-house), hydrochloric acid solution (37 %), sodium hydroxide pellets (98 % purity), calcium chloride (99.99 % purity) and commercial sodium metasilicate (95 %) were used as delivered in this study. The chemicals were purchased from Sigma-Aldrich and used as delivered without any modification or purification.

2.2. Methods

Firstly, the CFA was characterized using X-ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), proximate and particle size analysis. Then, the silica (SiO_2) content of the CFA was extracted via acid leaching using 3M hydrochloric acid (HCl) at 100°C for 6 hours. The extracted SiO_2 was filtered out, purified through successive demineralized water washings and dried in an oven at 200°C for 2 hours. The extracted silica was reacted with sodium hydroxide (NaOH) at 80°C and atmospheric pressure to produce sodium silicate. Physicochemical properties of the synthesized sodium silicate (CFA-Na_2SiO_3) were checked and compared to those of a commercial sodium silicate (com-Na_2SiO_3) using XRD and FTIR analyses.

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) (see Table 1). The $CaCl_2$ was added to enhance the solubility of the cement in the slurry. Densities, compressive strength, and rheological properties of the extended slurries using CFA-Na_2SiO_3 and com-Na_2SiO_3 were carried out according to the specification for materials and testing for Well Cements by American Petroleum Institute (American Petroleum Institute Specification 10A). Specifications for Cementing and Materials for Well Cementing, ANSI/API 10A/ISO 10426-1-2001 and compared. The slurries were pre-conditioned using an Atmospheric Consistometer prior to the rheology test. The bottom-hole circulating temperature (BHCT) used for the rheology tests was 52°C and the slurries were stirred for a period of 20 minutes at a speed of 150 rpm each. Parameters of the slurries such as shear thinning, plastic viscosity, apparent viscosity and yield stress were investigated. 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°C and a pressurized mud balance was used to determine the densities of the slurries 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 52ºC and pressure of 5000 psi.

Table 1 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. Results and discussion

3.1. Characterization of South African CFA

Table 2 shows the XRF results of the CFA from Power Station X compared with reports from literature [9-10]. 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 [9-11]. Interestingly, the CFA contains about 58 % SiO_2, the desired component for the synthesis of Na_2SiO_3.

Table 2. XRF analysis of CFA from Power Station X compared with literature

	% Composition		
Element	Power Station X CFA	Ref. [10]	Ref. [9]
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

The morphology of the CFA obtained from a SEM is depicted in Figure 1. The shapes of the CFA particles are determined by their exposure conditions (time and temperature) in the combustion chamber [12].

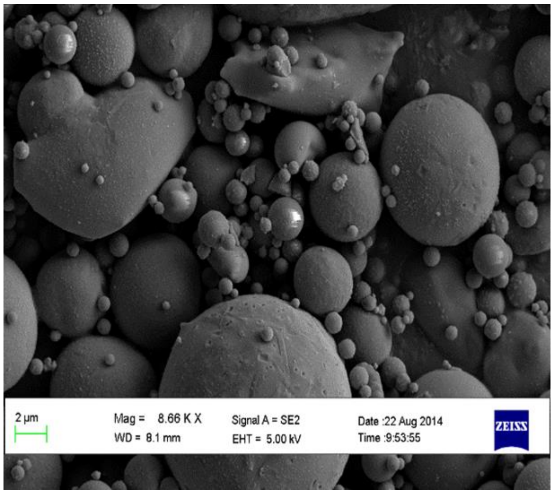

Figure 1. SEM micrograph of CFA

As seen in Figure 1, most of the particles are spherical, especially in the finer fractions. A similar observation has been reported [9-10]. The spheres, whose major components are opaque, are predominantly iron oxides and some silicates whilst the non-opaque spheres are mainly silicates [12]. 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) [10]. In addition, the SEM image shows the presence of some amorphous non-spherical particles which are mainly from incomplete combustion of coal components due to less exposure to high temperatures [12].

Furthermore, the TGA conducted on the CFA shows that the CFA contains about 0.2% moisture, 1.6% volatile matter and 1.7% fixed carbon. The particle size analysis shows that the particle size of CFA ranges from 0.32 – 112 µm. These results are in agreement with previous studies [9,11]. When the CFA was mixed with de-ionized water, a rise in pH from 7 to 10.7 was observed over a period of 5 hours, attributable to the dissolution of compounds such as CaO in the CFA. This observation is in good agreement with the literature [9].

3.2. Extraction of SiO_2 from CFA and synthesis of Na_2SiO_3

Morphologies of the extracted SiO_2 synthesized CFA- Na_2SiO_3 and com- Na_2SiO_3 were checked with SEM (Figure 2) and the images are in agreement with the image reported for precipitated SiO_2 [13]. Also, XRD patterns, Figure 2, of the SiO_2 reveal the characteristic slope and pattern for amorphous SiO_2 [13-16]. In addition, the FTIR spectrum of the SiO_2, Figure 3, shows bands of absorption at 1199 cm^{-1}, 964 cm^{-1} and 682 cm^{-1} attributable to the absorption peaks characteristic of SiO_2 [17]. Absorption peak at 1199 cm^{-1} corresponds to the asymmetrical stretching vibration of Si-O [13,15,17].

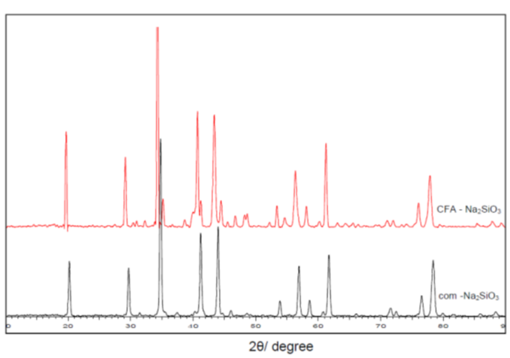

Figure 2. X-ray patterns of com-Na2SiO3 and CFA- Na2SiO3

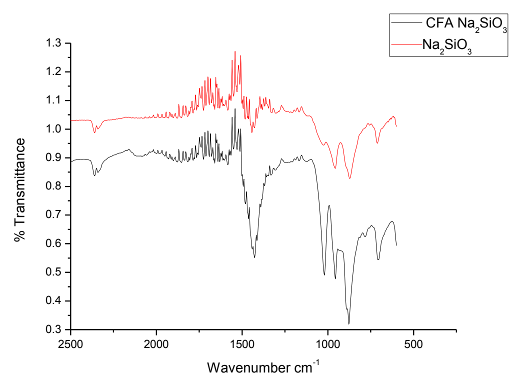

Figure 3. FTIR spectra of com-Na_2SiO_3 and CFA-Na_2SiO_3

The XRD patterns for CFA-Na_2SiO_3 and com-Na_2SiO_3 shown in Figure 2 are similar with a little difference in the intensities of some of the peaks. In addition, a slight shift in the peaks of CFA-Na_2SiO_3 was observed, and this could be attributed to the small quantity of the sample used in the analysis. FTIR analysis of the two samples indicates that there is no observable chemical difference in the samples (see Figure 3). The FTIR spectra 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 sodium metasilicate [18]. 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 [17].

3.3. Performance evaluation of the synthesized CFA-Na_2SiO_3 as OWC additive cement

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 3. 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 due to that slurries prepared using CFA-Na_2SiO_3 had much froth. Rheology of the slurries prepared using CFA-Na_2SiO_3 and com-Na_2SiO_3 as additives are shown in Table 4 and Table 5 respectively. The 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/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 3. Compositions and densities for OWC slurries

% Additive	Water (%)	Class G Cement (g)	Slurry density (ppg) (com-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

Table 4. Rheology of slurries prepared with com-Na_2SiO_3

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 5 Rheology of slurries prepared with CFA- Na_2SiO_3

	%CFA SS						
Rheology @ BHCT (rpm)	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
Pv (cp)	18	11.25	8.25	15.75	10.5	10.5	11.25
Yp (lb/100ft2)	13.5	32.25	15.75	21.25	20.5	34	29.25

The compressive strength results for slurries containing com-Na_2SiO_3 and CFA-Na_2SiO_3 at 8 hours, 12 hours and 24 hours are depicted in Figure 4, Figure 5 and Figure 6, respectively. The figures 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. In addition, the figures show that the CFA-Na_2SiO_3 slurries gained compressive strength of 50 psi earlier than the com-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.

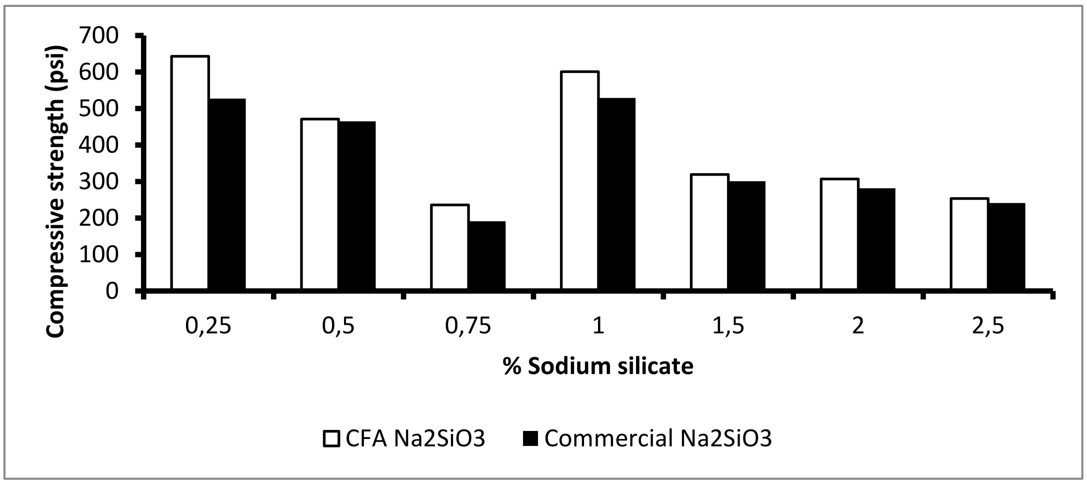

Figure 4. Compressive strength of OWC/sodium silicate at 8 hours

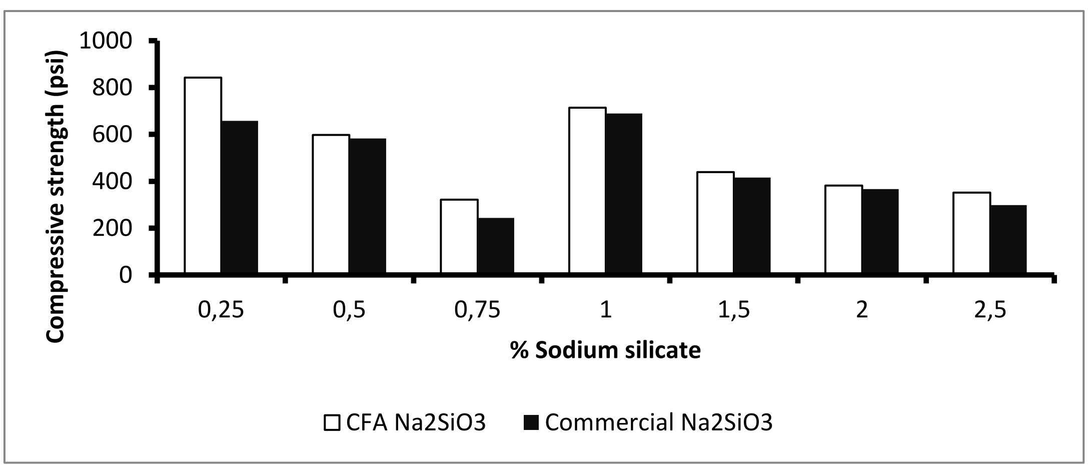

Figure 5. Compressive strength of OWC/sodium silicate at 12 hours

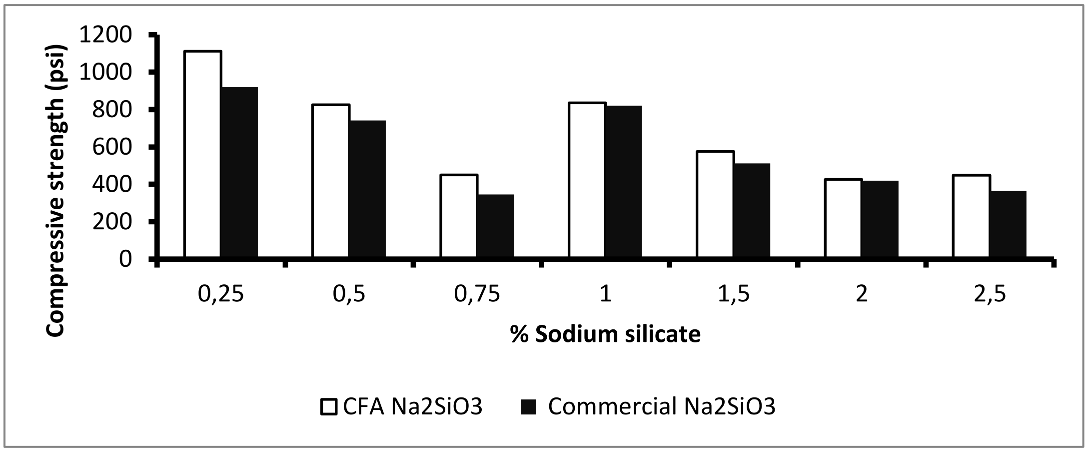

Figure 6. Compressive strength of OWC/sodium silicate at 24 hours

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 6). Furthermore, the slurries extended with CFA-Na_2SiO_3 are less viscous and have greater compressive strength compared to com-Na_2SiO_3 slurries. Although, evaluation of the thickening times of the slurries could not be carried out because the HPHT consistometer was faulty at the time of this study, however, results from rheology of the slurries indicate that CFA-Na_2SiO_3 slurries would be easier to pump and prefer where early strength development is critical.

4. Conclusions

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 physicochemical 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 prefer where early strength development is critical. It is worthy to note that the thickening time of the slurries could not be measured at the time when this study was carried out. Notwithstanding, this report could serve as a platform upon which further research development on the beneficiation of South African CFA in OWC and cementing operation could be built. Hence, this report opens up a way for the beneficiation of South African CFA in the petroleum, oil and gas industry.

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