A Pozzolanic Supplementary Material to Reinforce Class G Cement Used for Drilling and Completion Operations

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Abstract

There have been many studies to improve cement integrity under different pressure and temperature conditions where cement degradation is initiated by the mechanical and chemical interactions. Several approaches were presented so far to resolve this issue, many of which are either expensive or inefficient under certain circumstances. In this paper, attempts are made to show the application of Palm Oil Fuel Ash (POFA) as a cheap but efficient supplementary cementing material (SCM) for drilling and completions practices. A series of experiments were conducted to evaluate the changes in the density, free fluid, rheology, weight on cement, compressive strength, matrix structure and composition of the cement modified by POFA. The results obtained indicated that POFA has a hydrophilic surface and can retard pozzolanic reactions. It was appeared that POFA does not significantly change the rheology but may reduce the plastic viscosity. After 24 hours and 9 months of curing, 5 wt% POFA based cement appeared to have the highest compressive strength with a very consolidated matrix as observed through XRD, TGA and SEM tests. It was also revealed that nanosilica (NS) may significantly increase the plastic viscosity of the cement while POFA may give a higher strength to the cement in a long curing process. It was then concluded that POFA can be a very good choice to improve the mechanical strength and the matrix structure of the cement under different drilling conditions.

Keywords: Class G Cement, POFA, Nanosilica, strength enhancement, extender

1. Introduction

Cementing operation is performed during drilling and completion stage to isolate problematic intervals and prevent wellbore integrity due to mechanical and chemical interactions. As such, cement failure can easily result in catastrophic incidents such as blow-out, environmental contaminations, and partial or even total loss of wells.

There have been many attempts to improve cement integrity under different pressure and temperature conditions, where changing the water to cement ratio, adding Pozzolanic materials and altering the cement type have been proposed. However, many of these approaches are either expensive or partially successful when applied in a real field condition with extensive mechanical degradation (Carey et al., 2007; Aiken and Wildgust, 2009).

Palm Oil Fuel Ash (POFA) is the by-product of palm oil industry, generated from the burning of fibres, shells and empty fruit bunches in the palm oil mill boilers (Oyejobi et al., 2015). It is basically regarded as an agricultural waste that is largely available in tropical countries such as Malaysia. Given the fact that POFA is dominated by silica in its composition, there have been many attempts to show its application as a supplementary cementing material (SCM) in the civil industry. This could also help to reduce the amount of wastes disposed into the landfills (Subhashini and Krishnamoorthi 2016). For instance, Tay (1990) used ungrounded POFA to replace the cement in the concrete and concluded that due to the low pozzolanic activity, only 10 wt% of POFA should be used as a replacement. However, later researchers observed that the grounded POFA possess a good pozzolanic activity and can be used at a higher replacement level in concrete (Chindaprasirt and Rukzon 2009, Sukantapree et al., 2002, Tangchirapat et al., 2003). Ahmad et al., (2008) used different types of pozzolanic materials (e.g., POFA, fly ash and Quarry dust) and compared the results with a control sample. They observed that the cement based POFA with 15 wt% replacement was the best sample in terms of the compressive strength and workability. Bamaga et al. (2013) carried out a series of experiment on the concrete made by POFA and compared its performance with the control sample. They indicated that the strength in the POFA based concrete is developed at the later stage. However, sufficient resistance was observed once the concert was tested against the Cl^- ion penetration. Improvement in the sulphate resistance was also reported for the POFA based concreate and it was also concluded that POFA from different fields behave differently. Oyejobi et al. (2014) observed that by adding a small amount of POFA, the workability of the concrete and its resistance against the chemical attack improves. Moreover, reductions in the rate of hydration and chloride ion penetration was reported. Deepak et al. (2014) performed a series of experiments on the concrete samples with different quantities of POFA, ranging from 5 wt% to 45 wt%. They concluded that the best results in terms of mechanical properties (i.e., compressive, flexural, and tensile strength) are achieved when 15 wt% POFA is used. However, the author suggested that up to 25 wt% replacement can be made without posing any deleterious effects on the concrete strengths. Oyejobi et al. (2015) observed that the strength of the POFA based cement composites is lower than the control sample and the strength of the samples drop as the quantity of POFA increases. Subhashini and Krishnamoorthi (2016) observed that the best compressive, flexural, and tensile strengths are achieved with the cement composite bearing 20 wt% POFA. Having said that and to the best of our knowledge, POFA has not been properly introduced to the petroleum industry as a supplementary cementing material (SCM).

The aim of this paper is to perform a series of tests on the POFA based cement and highlight the potential applications of this waste as a cheap but efficient additive for the oil well cementing. An attempt was also made to compare the performance of POFA with nanosilica once added to the cement as a pozzolanic material.

2. Methodology

2.1. Cement Compositions

Class G cement was considered for the purpose of this study as it is commonly used in the oil industry during drilling and completion stages. The Blaine specific surface area of the Class G cement is about 280-340 m^2/kg (Kurdowski, 2014). POFA was obtained from the Lambir field of the Sarawak state in Malaysia and grounded for 8 hours in the ball mill to achieve the particle size of 12 microns. The physical and compositional characteristics of POFA are given in Table 1 and Table 2 respectively.

Table 1: Physical properties of POFA used for the purpose of this study

Colour	Specific Gravity	Particle retained on 45μm sieve (%)	Median particle D_{10}	Median particle D_{50}	Median particle D_{90}	Mean diameter	Surface area (cm^2 /g)	Soundness (mm)
Black	2.2	0.3	1.65	9.75	28.8	12.9	38,326.4	2.4

Table 2: Different oxide components in the structure of POFA obtained from XRF analysis

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	TiO_2	Na_2O	Loss on Ignition (LOI)
57.8	2.3	9.6	3.6	1.4	3.5	0.11	0.56	20.7

2.2. Sample Preparation

The standard procedure followed for the preparation of the POFA based cement was the American Petroleum Institute (API). This standard was chosen as it is commonly used in the industry for the preparation of primary and secondary cement. Different researchers (e.g., Barlet-Gouedard et al., 2006, 2009; Kutchko et al., 2007, 2008; Garnier et al., 2010; Brandl et al., 2010; Lesti et al., 2012; Zhang et al., 2014) also used the API standard for the preparation and testing of the oil well cement. The detailed instruction of the cement preparation and testing procedures used in this paper are given in the API 10-A and 10-B.

However, for the mixing of POFA with the cement, the literature approach presented by Ershadi et al. (2011) and Rahman et al. (2015) was followed since there was no instruction as to how POFA can be added to the cement based on the API 10-A or 10-B. As such, POFA and the cement were hand-mixed thoroughly for 5 minutes and added to water by a water to solid ratio of 0.44. The mixture was stirred for 3 minutes at the speed of 4000 RPM followed by a high-speed mixing at 12,000 RPM for 35 seconds. The blender used for the mixing of POFA based cement was Fann constant speed mixer. Different quantities of POFA were mixed by the class G cement. For the purpose of this study, different replacement levels of the cement with POFA were considered, ranging from 5 wt% to 20 wt% as given in Table 3. Figure 1 shows different cement samples prepared for the purpose of this study. It should be noted that nanosilica based cement were also used in this study for the comparison purposes while their preparation technique was comprehensively presented by Abid et al., (2018).

Table 3: Different POFA based cement composites used for the purpose of this study

Sample No.	Content of POFA (%)	Weight of POFA (g)	Weight of Cement (g)	Mix water (g)
1	0 (neat cement)	0 (neat cement)	692	305
2	5	34.6	657.4	305
3	10	69.2	622.8	305
4	15	103.8	588.2	305
5	20	138.4	553.6	305

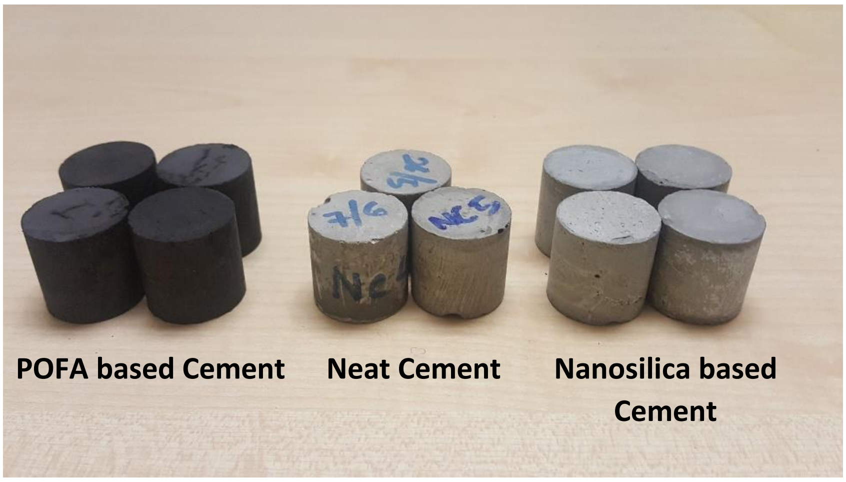


Figure 1: Different cement samples prepared for the purpose of this study

3. Experimental Results

3.1. Density

Density is defined as the weight of the solid/fluid per unit volume. To measure the absolute density of the cement samples, Fann Mud Balance TruWate Model 141 was used. The pressurized mud balance cup is able to remove air bubbles and provide accurate recordings close to the density under the downhole condition. The density and specific gravity of POFA based cement are reported in Table 4.

Table 4: Density and specific gravity of POFA based cement

POFA content (BWOC)	Density (ppg)	Specific Gravity
0 (Neat Cement)	15.5	1.86
5	15.2	1.82
10	15.3	1.84
15	15.3	1.84
20	14.8	1.77

As it is seen in this table, the density of the POFA based cement is very close to the neat cement. In fact, the density remained the same for all the samples except the one with 20 wt% POFA, which has a lesser density than others. This could be due to the low specific gravity of POFA (2.2) which may cause weight reduction once mixed with the Class G cement (specific gravity of 3.15) in a high concentration (Khankhaje et al., 2016, Sooraj, 2013). It was concluded that POFA can be used as an extender to reduce the density of the cement slurry in the intervals where lost circulation is encountered.

3.2. Free Fluid Test

Free Fluid test was conducted according to the API 10-A standard. According to this standard, after the preparation of the cement slurry, it should be conditioned using a Consistometer at the temperature of 27°C for 20 min. Since the base cement used was class G cement, the mass of the cement that should be transferred into the dry 500ml conical flask is 760±5 g. This mass was recorded and the mouth of the conical flask was sealed with the self-sealing film. The flask was then placed on a vibration free surface for 2 hours. Subsequently, the supernatant fluid was removed with a syringe and measured by the accuracy of ±0.1 ml using the following equation:

$$FF = \frac{V_{ff} \times \rho}{m_s} \times 100 \tag{1}$$

where FF is the free fluid content, V_{ff} is the volume of the supernatant fluid collected, ρ is the specific gravity of the slurry and m_s is the mass transferred to the conical flask. Applying this equation, the free fluid percentage of the POFA based cement was obtained and summarised in 5. Figure 2 shows the collection of the supernatant fluid as part of the free fluid test.

Table 5: Percentage of free fluid in the POFA cement composites

POFA Content (%)	Mass Transferred (g)	Specific Gravity	Volume of Supernatant fluid (ml)	Free Fluid (%)
0 (Neat Cement)	763.3	1.86	11.5	2.80
5	766.8	1.82	11.15	2.65
10	766.6	1.84	9.5	2.28
15	766.11	1.84	7.5	1.80
20	763.23	1.77	7.2	1.67

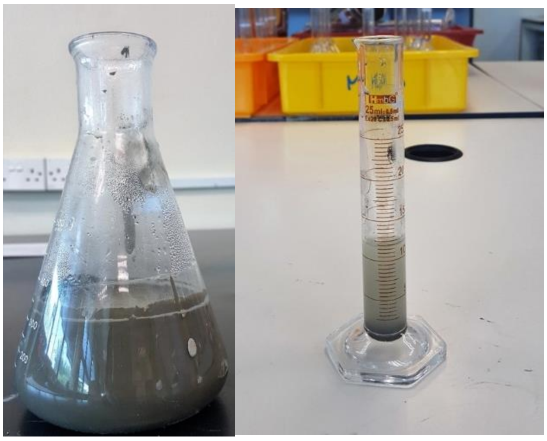


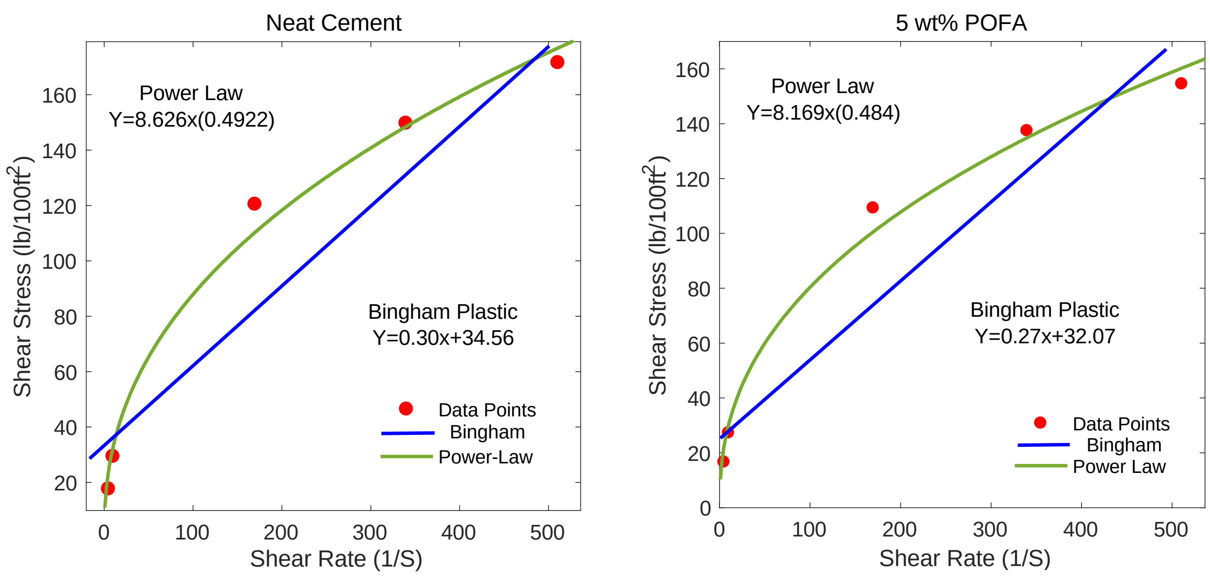
Figure 2: Collection of the supernatant fluid for the free fluid test

Summarised in Table 5, as the quantity of POFA increases in the cement slurry, the amount of free fluid decreases. In fact, the percentage difference between the neat cement and the POFA based cement could reach up to 50%. This indicates the fact that POFA has a hydrophilic nature and absorbs water. However, all POFA cement composites pass the threshold limit stated in the API 10-A standard which emphasises that the percentage of the free fluid of the cement slurry should not exceed 5.90%. It should be noted that the lower limit of the free fluid is basically based on the viscosity of the cement designed.

3.3. Rheology

Rheology of the cement is an important parameter indicating the horse power required and the frictional loss induced during the cement placement. Three commonly used mathematical models for determination of the rheological behaviour of the cement are Bingham plastic, Power law and Herschel-Buckley models. Among these three, Bingham plastic is the primary model due to its linear nature and proven applications. Plastic viscosity and yield point are the slope and intercept of the graph created after plotting the shear rate against the shear stress in the Bingham law. On the other hand, the power law model is represented by two parameters, consistency index (k) and behaviour index (n), which respectively indicates the apparent viscosity and the degree of the non-Newtonian behaviour in the cement slurry. Herschel-Buckley is also a reliable mathematical model which is also known as the Yield Power Law. It is basically a combination of the Power and Bingham laws which include the effect of the yield stress in the Power law model. As such, it has three parameters including the yield stress (as the intercept) together with the parameters n and k which are identical to those obtained from the Power law model (Hemphill et al., 1993, Ugochukwu 2015).

For determination of the rheological behaviour of the POFA based cement, the API 10-B standard was followed. The rotational viscometer of Fann model 35 was used to obtain the parameters of the Bingham and Power law models whilst an atmospheric consistometer was used to condition the cement samples for 30 min at the temperature of 50°C. The readings were taken at different rates except 600 rpm since it could pose unfavourably changes to the cement properties. The results obtained from the rheological measurements of the POFA based cement are summarised in Figure 3, Figure 4 and Table 6. It should be noted that each test was repeated twice for the same cement composition to ensure the consistency of the results.



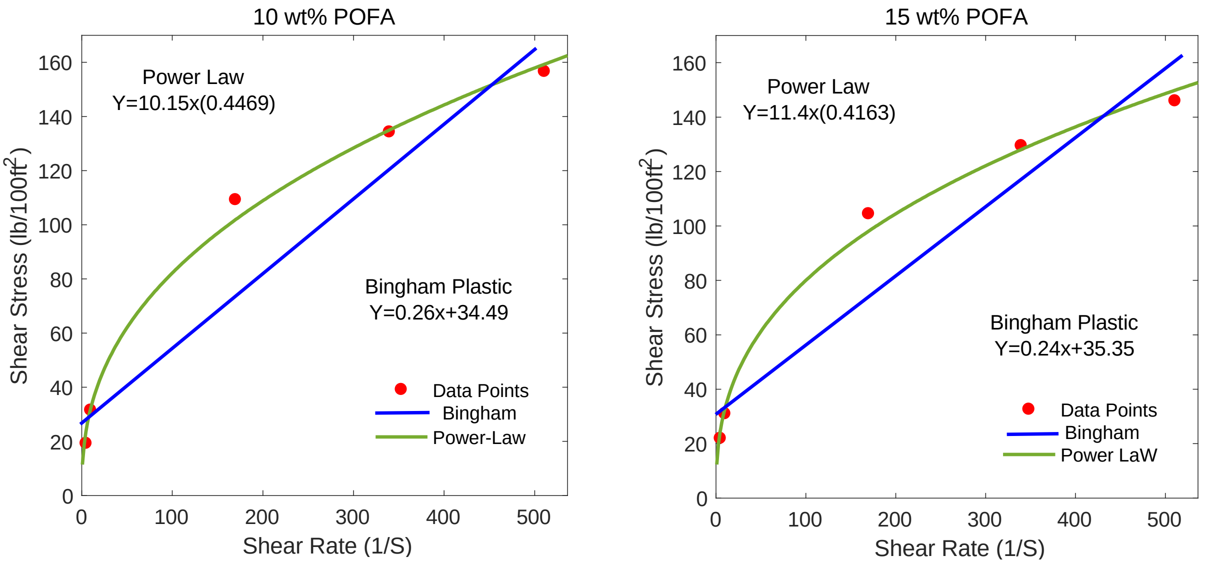


Figure 3: Rheological behaviours of the neat cement and POFA based cement composites described by the Power-law and Bingham Plastic models

Table 6: Rheological models and the parameters of the POFA cement composites

		Herschel-Buckley		
	Bingham Plastic		Power Law	
POFA Content (%)	Plastic Viscosity (cP)	Yield Point (lb/100ft^2)	n	k (lb-sec/100ft^2)
0	145.74	34.56	0.49	8.62
5	131.33	32.071	0.48	8.16
10	128.46	34.50	0.45	10.15
15	118.12	35.35	0.42	11.47
20a	124.58	34.03	0.46	9.15
20b	127.8	36.03	0.44	10.57

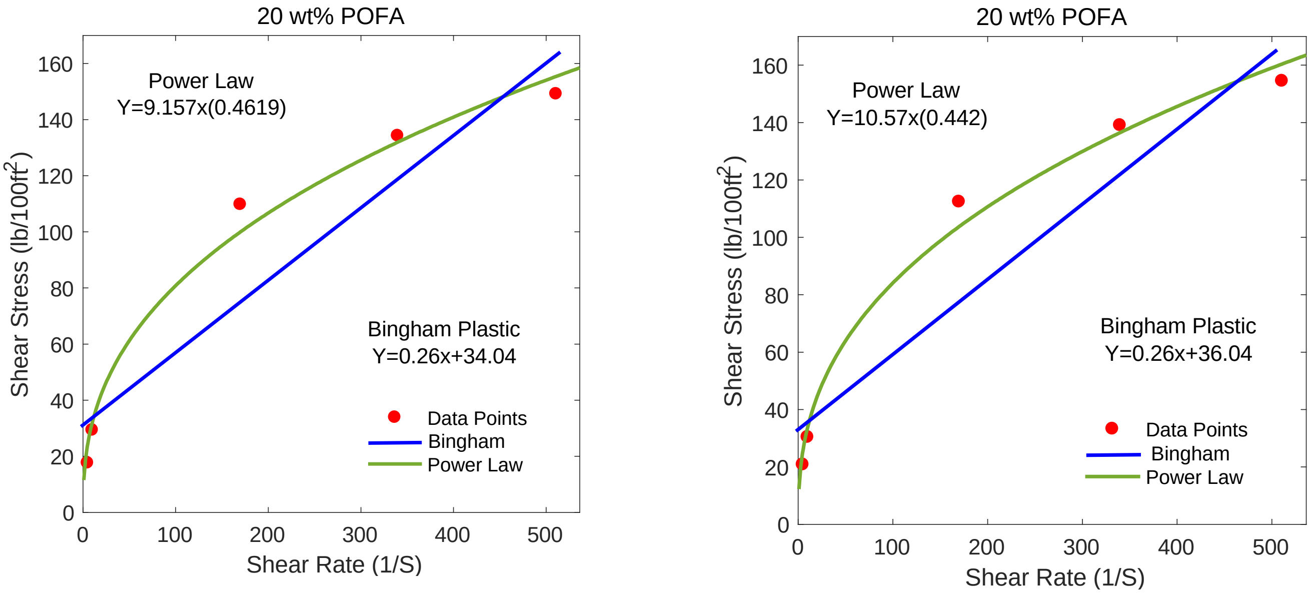


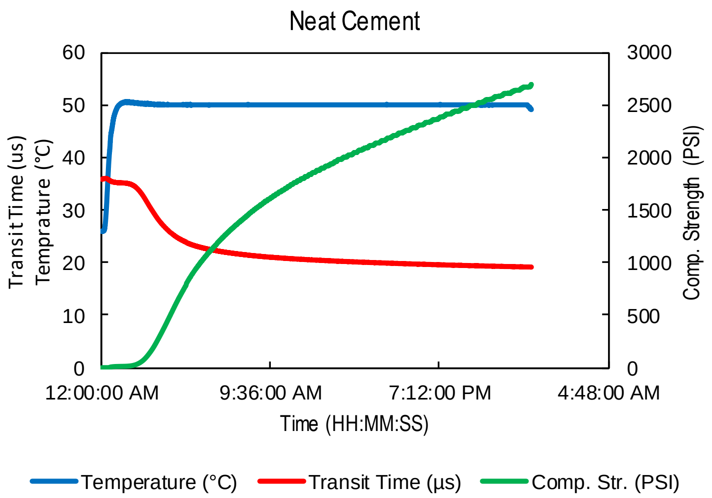
Figure 4: Comparison between the rheological behaviour of two cement composites with 20wt% POFA

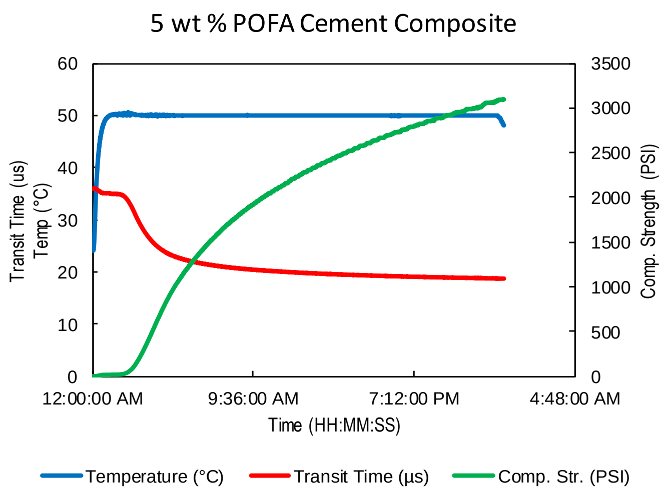
Looking at Figure 3 and 4 and Table 6, it was appeared that the Herschel-Buckley is the best rheological model to explain the behaviour of the cement considering its ability to fit a power type curve to the data with a yield point intercept. The rheological measurements of the POFA based cement also highlighted that the plastic viscosity and the yield point of the neat cement is higher than all POFA based cement composites. The decrease in the rheological properties of the samples could be linked to the fact the POFA is a pozzolanic material and acts as a filler. According to the recent studies, pozzolanic fillers will improve the workability of the cement, decrease the thermal and shrinkage cracking, and emits low heat of hydration (Ye et al., 2007, Poppe and De Schutter, 2005). They also improve the particle distribution in the powder skeleton, decrease the interlayer friction and give a good density packing to the structure of the cement (Elyamany et al., 2014). It was also interesting to see that even with a lower viscosity, the thickening time of the POFA based cement was not negatively impacted. In fact, according to the WOC test results, which will be discussed in the next section, the POFA based cement except the one with 20 wt% POFA would achieve the strength of 500 PSI faster than the neat cement.

3.4. Compressive Strength

3.4.1. Non-Destructive Test

Compressive strength is an important parameter in the cement design which indicates the maximum load sustained by the consolidated cement before failure. For determination of the compressive strength in real time, Fann Ultrasonic Cement Analyser (UCA) Eurotherm Model 3504 was used. This apparatus is capable of providing an initial set time (i.e., the time required for the cement to achieve the compressive strength of 50 PSI) and Weight on Cement (WOC) (i.e., the time needed for the cement to reach the compressive strength of 500 PSI). The tests were carried out for 24 hours at the temperature and pressure of 50°C and 2200 PSI (15MPa) respectively for all POFA cement composites. The results obtained are shown in Figure 5 and Table 7.





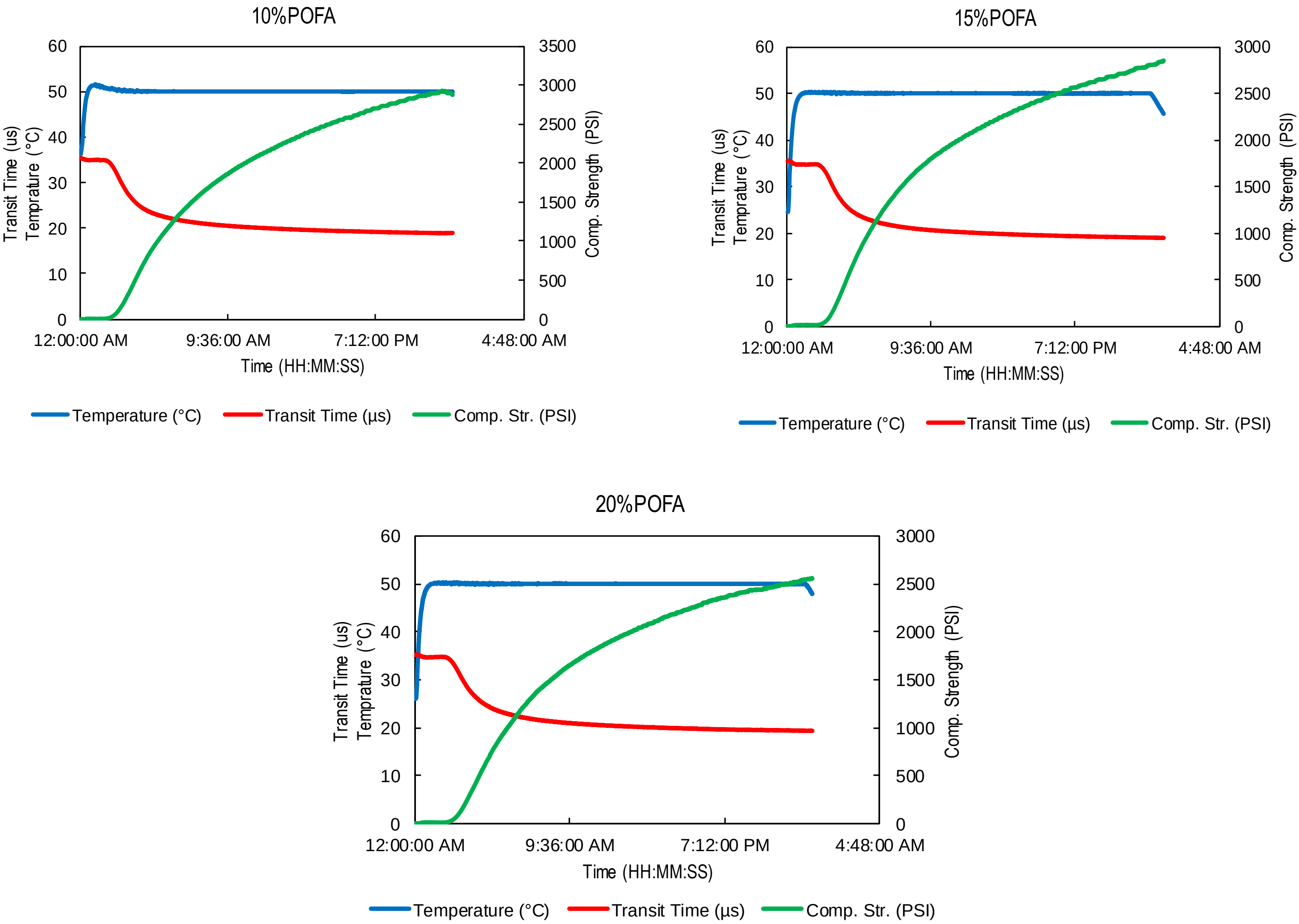


Figure 5: Compressive strength of different POFA cement composites obtained from UCA

Table 7: Compressive strength of different cement composites after 24 hours

Time (Hours)	Neat Cement (PSI)	5% POFA (PSI)	10% POFA (PSI)	15% POFA (PSI)	20% POFA (PSI)
4	533.42	660.535	683.46	567.241	504.1
8	1397.40	1604.935	1633.70	1547.67	1438.64
12	1831.43	2097.41	2128.52	2011.68	1889.38
16	2137.62	2445.84	2473.16	2327.81	2181.01
20	2409.38	2730.325	2713.91	2537.54	2398.91
24	2647.87	2919.735	2891.74	2720.49	2537.96

The results obtained indicated that after 24 hours of curing in the UCA, the compressive strength of the POFA based cement is higher than the neat cement except the one with 20wt% POFA. However, it seems that as the quantity of POFA increases, the strength of the cement decreases. This decrease in the compressive strength could be linked to the replacement of POFA which reduces the amount of C-S-H and Portlandite in the cement matrix (Karim, et al. 2011). It was concluded that 5 wt% replacement of the cement by POFA gives the best compressive strength, but up to 15 wt% replacement can be done without having any deleterious effects on the compressive strength. Table 8 gives the results obtained from the WOC measurements.

Table 8: Weight on Cement (WOC) determined for the POFA based cement composites

POFA Content (%)	WOC (HH:MM: SS)
0 (Neat Cement)	03:54:11
5	03:34:57
10	03:32:07
15	03:45:11
20	03:59:21

Looking at Table 8, it was appeared that the WOC of 5 wt% to 15 wt% POFA based cement is shorter than that of the neat cement. In fact, there is almost 20 min difference between the WOC of 5 wt% POFA with that of the neat cement which can reduce the Non-Productive Time (NPV) significantly.

3.4.2. Destructive Test

Destructive tests for the measurement of the compressive strength were carried out by a semi-automatic triaxial testing machine. The samples used for the measurements had a cylindrical shape with a length to dimeter ratio of 1 as shown in Figure 1. The curing was done at the temperature of 50°C and at atmospheric pressure for one day followed by subjecting the samples to the ambient condition for a total period of 9 months. The loading rate was fixed at 18kN/min and the compressive strength of the cement were recorded as shown in Figure 6. The destructive test was not conducted on the 20 wt% POFA based cement due to its low compressive strength development recorded by the UCA after 24 hours.

It was then concluded that the sample with 5 wt% POFA has a higher compressive strength than the ones with 10 wt% and 15 wt% POFA. It was also found that the compressive strength of the cement with POFA increases as a matter of time due to the hydration of the cement which leads to the production of Portlandite and secondary C-S-H. However, as the quantity of POFA increases, the compressive strength decreases since C_3S and C_2S are removed from the cement matrix. This is the same conclusion made by Khankhaje et al. (2016) who indicated that as the quantity of POFA increases, the compressive strength of the concrete decreases.

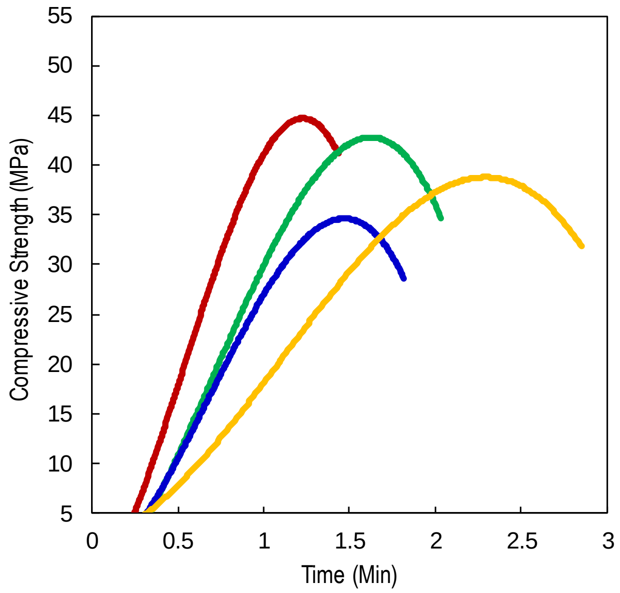


Figure 6: Compressive Strength of neat (yellow), 5 wt% POFA (maroon), 10 wt% POFA (green), 15 wt% POFA (blue) cement samples

3.5. Thermogravimetric Analysis

Characterization of the cement was done through Mettler Toledo Thermogravimetric Analysis (TGA). The working principle of the TGA is based on the weight loss of the sample when it is subjected to the heat. In this study and for the characterization of the POFA based cement, the weight loss due to the dehydroxylation of Portlandite was targeted. It should be recalled that as Portlandite consumes due to the pozzolanic reactions, the compressive strength increases. Considering the fact that POFA is a pozzolanic material, it was expected to have Portlandite reduction and a good compressive strength development in the cement samples. According to the literature, the temperature at which the dehydroxylation takes place varies from 400 to 500°C when the nitrogen flow rate is fixed at 50 ml/min (Lim and Mondal, 2015). To measure the quantity of Portlandite left in the samples, the following equation was used (Jain and Neithalath, 2009; Lim and Mondal, 2015):

$$CH\ (\%) = WL_{(CH)}\ (\%) * MW_{(CH)}/MW_{(H)} \quad (2)$$

where $WL_{(CH)}$ is the percentage loss of Portlandite during dehydroxylation, $MW_{(CH)}$ is the molecular weight of Portlandite and $MW_{(H)}$ is the molecular weight of water.

To do the TGA, the cement samples exposed to the reservoir condition in the UCA were chosen. It was then found that the least amount of Portlandite left in the samples belongs to 5 wt% POFA cement. The TGA results of the samples after 1 day of curing in the UCA are shown in the top left side of Figure 7 and summarised in Table 9.

Table 9: Percentage of Portlandite left in the samples after 1 day of curing in UCA

POFA Content (%)	Weight loss (%)	Portlandite (%)
0 (Neat Cement)	2.87	11.80
5	2.13	8.74
10	2.25	9.23
15	2.32	9.56
20	1.83	7.51

From Table 9, it can be concluded that the least amount of Portlandite was in the sample with 20 wt% POFA due to the significant amount of the cement replacement. Neglecting the results obtained from the 20 wt% POFA based cement, it was observed that the least amount of Portlandite left in the samples belongs to the cement with 5 wt% POFA. This is aligned with the results obtained from the non-destructive tests where it was indicated that the compressive strength of 5 wt% POFA based cement is higher than any other cement prepared. This is mainly because of the pozzolanic reactions induced by POFA and the reduction of Portlandite in the cement.

3.5.1. Curing age

To further assess the best cement composition, TGA was done on 5 wt% POFA based cement cured under similar conditions for one day and one month. The results obtained indicated that the weight loss after one month of curing is around 2.390% and the amount of Portlandite left in the sample is 9.82%. On the other hand, the Portlandite left in the cement after 1 day of exposure was 8.743%. The increase in the quantity of Portlandite after 1 month of curing revealed that as time passes and the hydration of the cement continues, more Portlandite is produced and the pozzolanic reaction takes place due to the presence of POFA. To further confirm these results, one more test was done on the sample with 10 wt% POFA. It was then observed that Portlandite left in the sample after 1 month of curing appeared to be 2% higher than the cement with 1 day of curing. The results of these tests are shown at the bottom of Figure 7.

3.5.2. Curing Condition

To show the effect of pressure and temperature on the hydration rate of the cement, two sets of samples with similar physical characteristics were chosen. One set was exposed to the temperature of 50°C and the pressure of 2200 PSI whilst the other set was placed in the water bath at the temperature of 50°C and atmospheric pressure. Both sets were cured for 24 hours before subjecting them to the TGA. The results obtained from this analysis on the neat cement are shows at the top right side of Figure 7.

As shown in Figure 7, the amount of Portlandite left in the neat sample cured by the UCA is higher than that of the water bath. This can be attributed to the effect of the pressure that have accelerated the hydration rate and increased the amount of Portlandite in the sample.

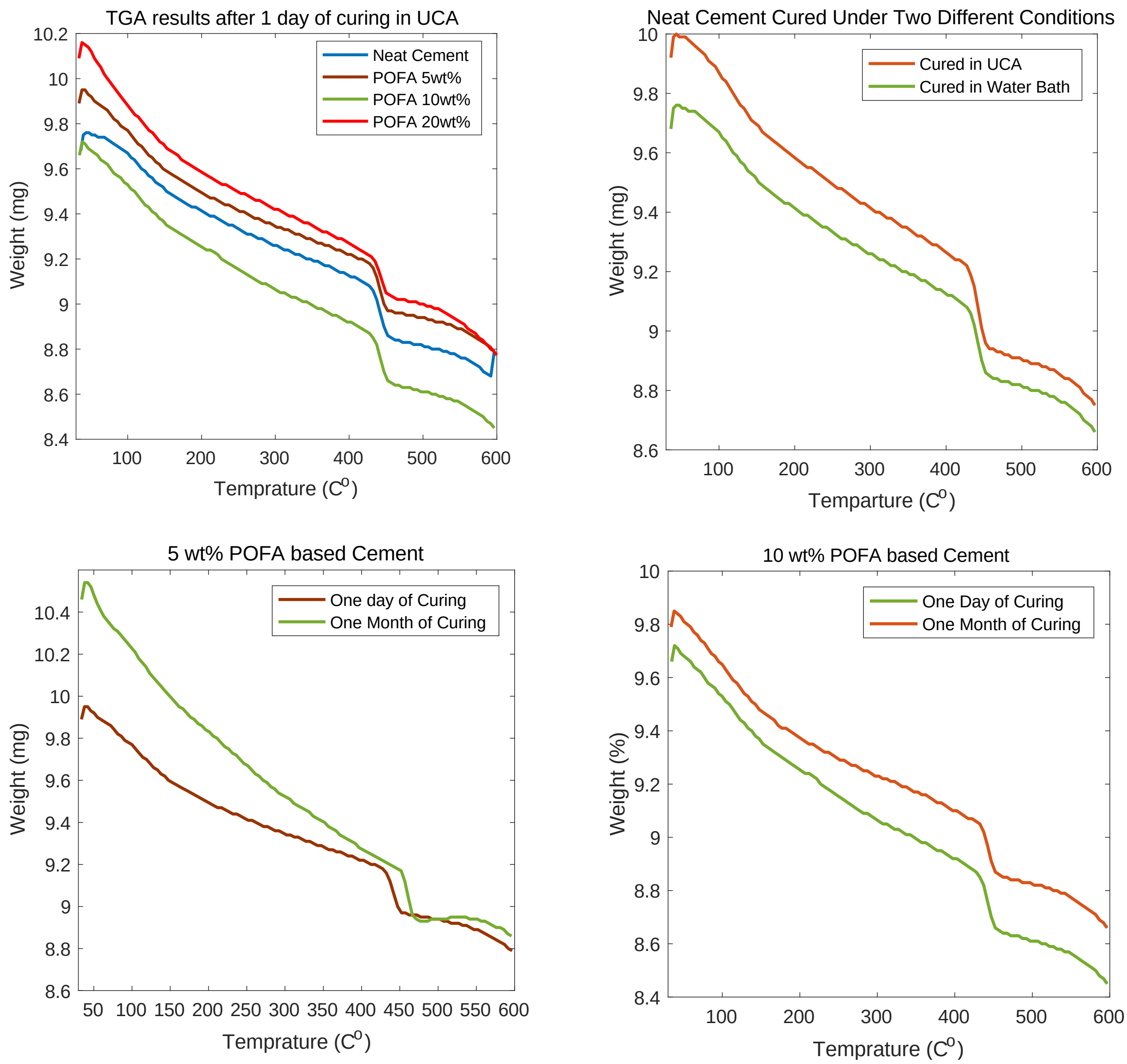


Figure 7: Weight loss of the cement samples under different curing conditions obtained from the TGA tests

3.6. XRD analysis

To further evaluate the amount of Portlandite left in the samples, XRD analysis was conducted on the neat, 5 wt% and 20 wt% POFA based cement. It was then observed that even after 6 months of curing, the amount of Portlandite left in 5 wt% POFA based cement is less than the neat cement. However, the least amount of POFA was in the sample with 20 wt% POFA which was mainly because of the high replacement level. The results obtained from the XRD analysis are shown in Figure 8 and summarised in Table 10. It should be noted that the high value of Portlandite observed in the table is due to the fact that XRD analysis can only determine the percentage of the crystalline (Portlandite) phases in the cement structure not the amorphous phases such as C-S-H.

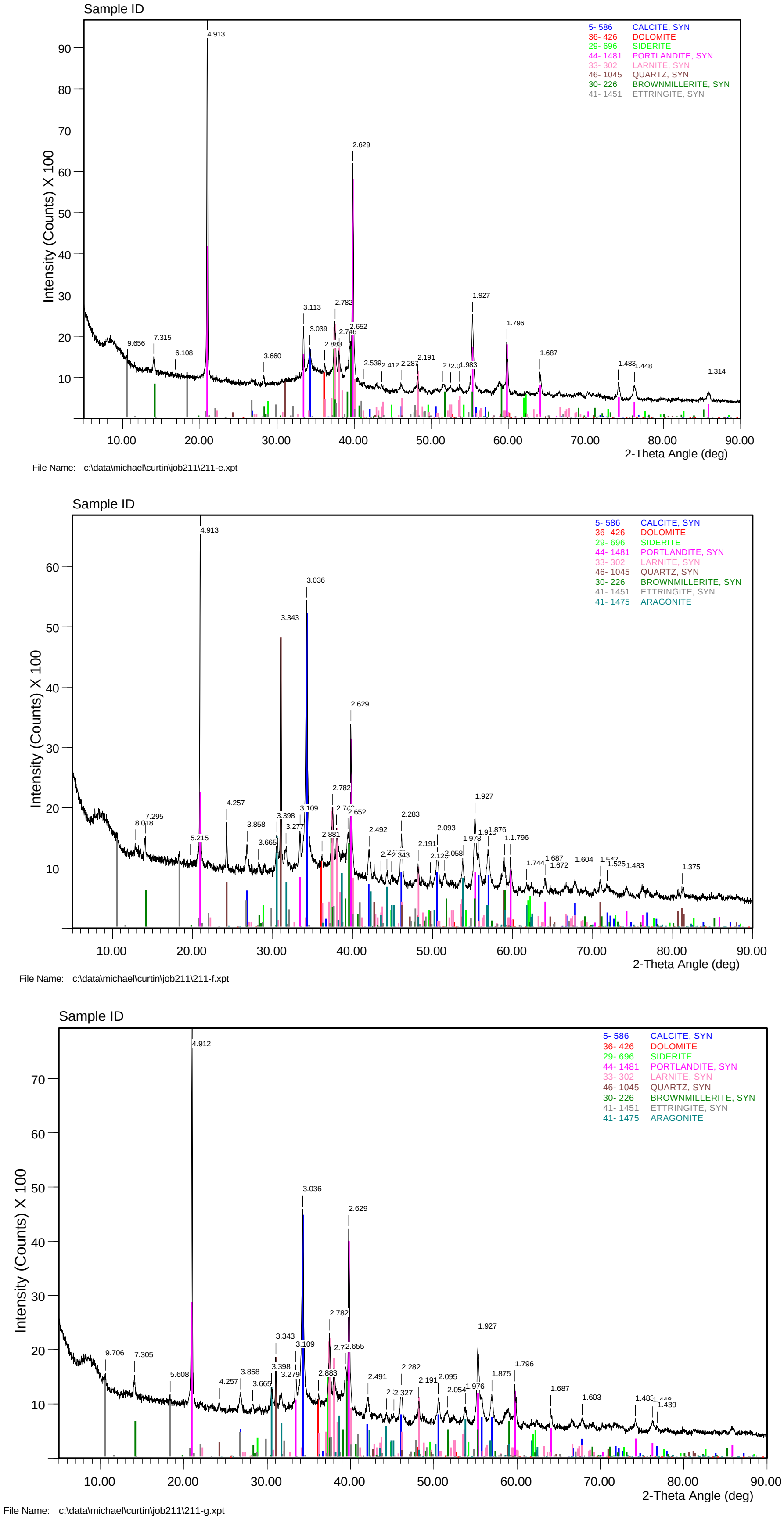


Figure 8: From top: XRD analysis of neat, 5 wt% and 20 wt% POFA based cement after 6 months of curing

Table 10: Amount of Portlandite left in the samples after 6 months of curing

RIR method	
Cement Composite	Portlandite (%)
Neat Cement	66
5% POFA	43
20% POFA	32

3.7. SEM Analysis

To analyse the surface structure and matrix consolidation of the samples, Scanning Electron Microscope (SEM) analysis was done on two samples with the lowest and highest amount of POFA. The results obtained, which are shown in Figure 9, indicated that the cement with 5 wt% POFA has a more densified and smoother surface compared to 20wt% POFA based cement.

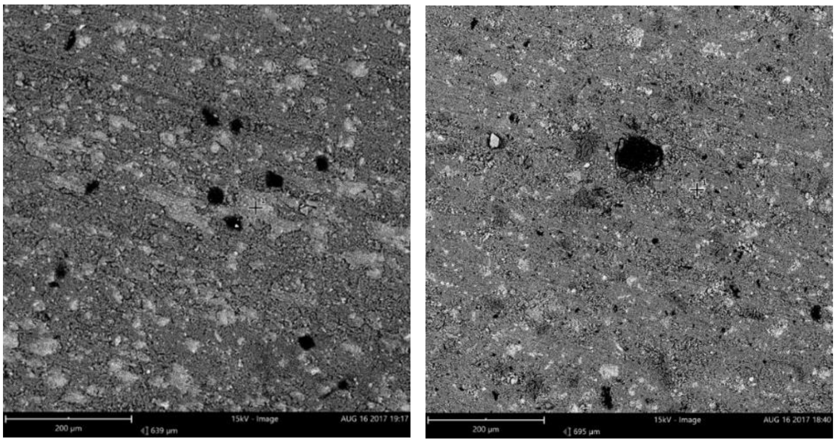


Figure 9: SEM analysis of 5% POFA cement composite (left) and 20% POFA cement composite (right)

To evaluate the effect of the curing condition on the cement matrix, two set of samples cured in the UCA and water bath for 24 hours were chosen. Both of these samples were exposed to the atmospheric condition for 6 months after the initial curing. The results obtained are shown in Figure 10.

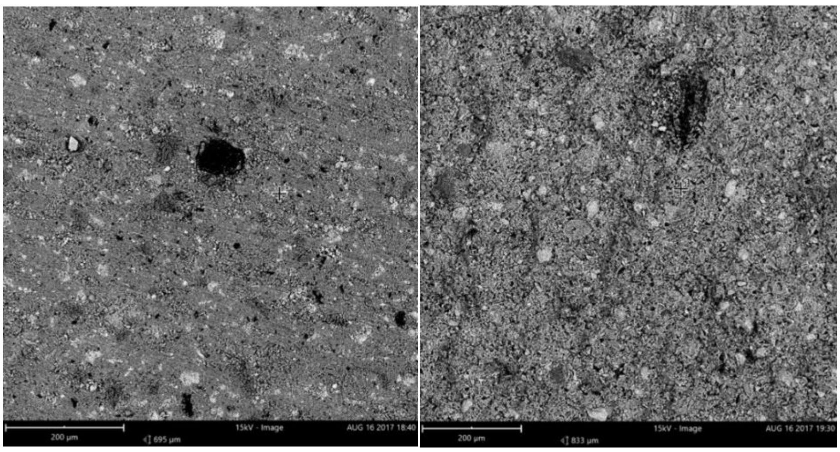


Figure 10: SEM of 20 wt% POFA based cement cured in the UCA (left) and water bath (right)

Looking at Figure 10, it can be concluded that a highly densified cement matrix is obtained when the samples are cured under high pressure and temperature conditions. This is linked to the changes in the hydration rate and the morphology of the cement matrix.

Considering the results obtained through different tests, it was appeared that POFA can be considered as a good pozzolanic material to improve the compressive strength without having detrimental effect on the density, rheology, composition and free fluid of the cement. Thus, in the next section, attempts were made to compare the performance of the cement samples produced by POFA replacement with those that have nanosilica in their structure. It should be noted that nanosilica is one of the best pozzolanic materials which can significantly increase the compressive strength of the cement upon proper mixing (Abid et al., 2018). This comparison is provided and discussed in the next section.

4. Nanosilica versus POFA Based Cement

Nano Silica (NS) were used in several studies to improve the strength and physical properties of the cement for HPHT and CO_2 sequestration sites (Barlet-Gouedard, et al. 2012). Like POFA, nanosilica is a pozzolanic material and its addition to the cement initiates pozzolanic reactions which can ultimately changes the composition, rheology and the strength of the cement. In this section, the performance of these two pozzolanic materials are compared by performing a series of density, rheology, compressive strength, XRD and Thermogravimetric tests. This may help to further understand the application of POFA in the oil well cementing.

It should be noted that nanosilica based cement samples used in this study were prepared according to the new mixing (sonication dispersion) method presented in the study of Abid et al. (2018). As such, the preparation procedure of the samples is not discussed in this paper.

4.1. Density

Measurements of the density of the samples were done using the same procedure presented earlier with the results reported in Table 11. According to this Table, there is not that much of differences between the density of the POFA and NS based cement with that of the neat cement.

Table 11: Density of NS and POFA based cement

NS (POFA) Content (%BWOC)	Density of NS cement (PPG)	Density of POFA cement (PPG)
0 (Neat Cement)	15.5	15.5
0.25 (5)	15.4	15.2
0.5 (10)	15.3	15.3
0.75 (15)	15.4	15.3
1 (20)	15.3	14.8

It should be noted that only a slight amount of nanosilica was added to the cement and as such the density remained the same as of the neat cement. Considering the cost of using nanomaterials, this slight amount would be feasible for deep and large projects.

4.2. Rheology

The plastic viscosity and the yield point of the nanosilica based cement were determined using the Bingham law and compared with those of the POFA based cement as reported in Table 12.

Table 12: Rheological properties of the NS and POFA cement composites

NS (POFA) Content (%BWOC)	Plastic Viscosity of NS cement (cP)	Plastic Viscosity POFA cement (cP)	Yield Point of NS cement (lb/100ft^2)	Yield Point of POFA cement (lb/100ft^2)
0	145.74	145.74	34.56	34.56
0.25 (5)	139.28	131.33	32.157	32.071
0.5 (10)	143.3	128.46	38.93	34.496
0.75 (15)	145	118.2	38.24	35.35
1 (20)	153.8	124.58	40	34.039

From Table 12, it can be seen that adding more than 0.75 wt% nanosilica increases the plastic viscosity of the cement even higher than that of the neat cement, which may not be favourable. Unlike nanosilica, the POFA based cement provided a lower plastic viscosity compared to the neat cement. An opposite trend was observed for the POFA and nanosilica based cement in terms of the rheological changes. This discrepancy might be related to the particle size since the size of nanosilica used in this study was between 15 to 20 nm whilst that of POFA was 12 microns. Therefore, nanosilica had a higher surface area and was much reactive than POFA. It should also be recalled that nanosilica is more hydrophilic than POFA and will absorb more free water, which ultimately increases the plastic viscosity of the cement.

4.3. Compressive Strength

The compressive strength of the cement bearing POFA and nanosilica was determined using the UCA machine. The measurements were done for 24 hours at the temperature of 50°C and pressure of 2200 PSI. Table 13 and Figure 11 compares the compressive strength development in the POFA and nanosilica based cement.

Table 13: Compressive strength of the POFA and nanosilica based cement after 24 hours of curing

Hours	Neat Cement	5% POFA	10% POFA	15% POFA	20% POFA	0.25% NS	0.50% NS	0.75% NS	1% NS
4	533.42	660.535	683.46	567.241	504.1	656.44	645.98	661.895	742.42
8	1397.40	1604.935	1633.70	1547.67	1438.64	1543.82	1582.59	1496.43	1578.71
12	1831.43	2097.41	2128.52	2011.68	1889.38	2058.71	2114.92	1977.7	2074.31
16	2137.62	2445.84	2473.16	2327.81	2181.01	2445.91	2506.75	2326.66	2449.09
20	2409.38	2730.325	2713.91	2537.54	2398.91	2739.78	2794.9	2610.77	2735.17
24	2647.87	2919.735	2891.74	2720.49	2537.96	2955.99	3019.82	2837	2980.75

From Table 13 and Figure 11, it is seen that the best compressive strength belongs to the sample with 0.5% nanosilica (i.e., 3019.82 PSI) followed by the sample with 5 wt% POFA (2919.73 PSI) with the difference of 100 PSI. It was interesting to see that unlike the samples with POFA, the compressive strength of nanosilica based cement increased as the amount of nanosilica increased. However, this trend starts to decline after adding more than 0.5 wt% nanosilica. This decrease in the compressive strength of the nanosilica cement composites was not as much pronounced as that of the POFA's though. It was also observed that both categories of the cement have a higher strength than the neat cement except the one with 20 wt% POFA. In the next stage, it was attempted to evaluate the strength of the cement after nine months of curing through the destructive tests. The results obtained are given in Table 14 and Figure 12.

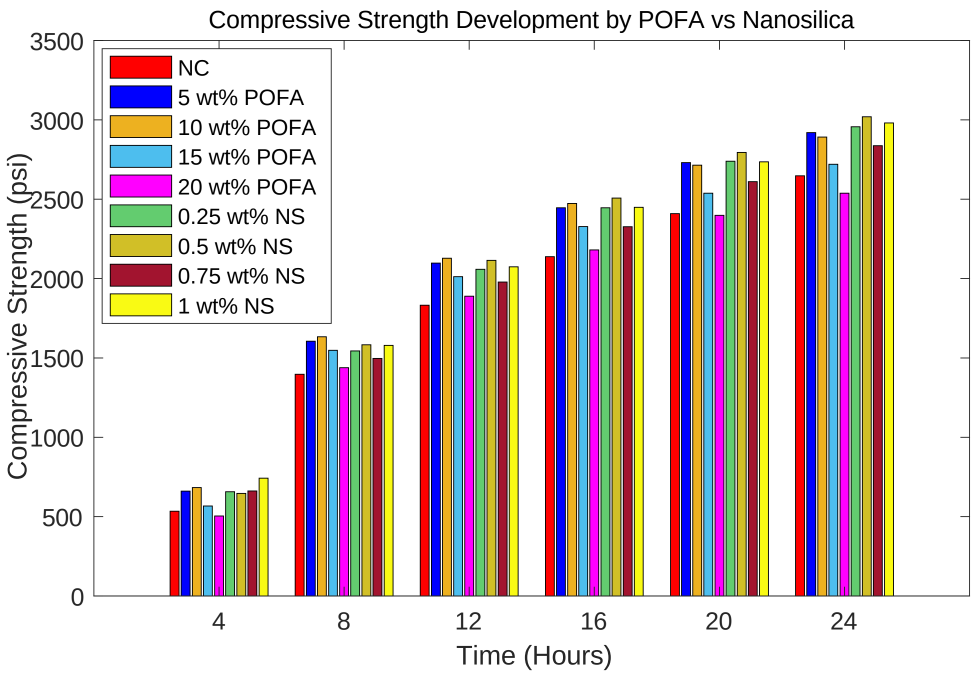


Figure 11: Compressive strength of NS and POFA based cement after 24 hours of curing

The results of the destructive tests conducted on the cement cured for 9 months revealed that the highest strength is achieved by the sample with 5 wt% POFA whilst the highest strength of the nanosilica based cement was achieved by the sample with 0.75 wt% nanosilica. This strength development in the cement could be due to the fact that there might not be enough Portlandite in the initial stage of hydration for the reaction with silica but as the aging continues, hydration of C_2S and C_3S produces Portlandite and enhances the pozzolanic reaction as shown in Figure 12.

Table 14: Compressive strength of different cement composites after 9 months of curing

Cement Composite	Comp. strength (MPa)
5%POFA	46.185
10%POFA	44.816
20%POFA	37.59
0.25%NS	34.65
0.5%NS	37.18
0.75%NS	43.5
1% NS	43.40

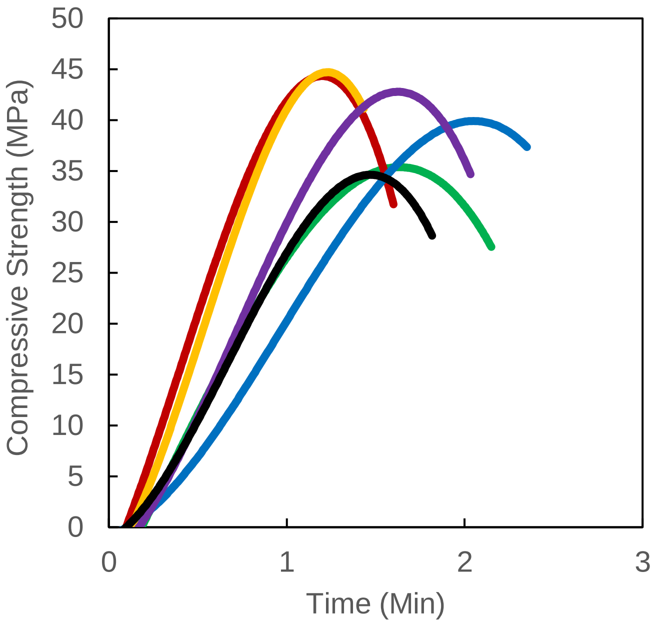


Figure 12: Compressive Strength of 5 wt% POFA (maroon), 10 wt% POFA (purple), 20 wt% POFA (black), 0.25 wt% NS (green), 0.75 wt% NS (red) based cement

The results obtained from the destructive and non-destructive tests indicated that POFA acts as a strength retarder and the strength development continues months after the placement. This was aligned with the results reported by Bamaga et al. (2013), where it was found that addition of POFA to concretes retards the compressive strength development. On the other hand, nanosilica acts as an accelerator in the development of the compressive strength. These behaviours could also be linked to the replacement level of nanosilica and POFA. In fact, POFA had a higher replacement level than nanosilica and, as such, more silica was injected in the cement which helped to gain the compressive strength at the later stage of hydration. However, it should be remembered that replacement beyond a certain threshold will saturate the cement slurry and the strength decreases when POFA or any other pozzolanic materials are added.

4.4. Thermogravimetric Analysis

Considering the fact that the best result in terms of rheology and strength was achieved by replacing 5 wt% POFA and 0.5 wt% nanosilica in the cement matrix, these two samples were chosen for the TGA analysis. As both of the additives were pozzolanic materials, it was expected to see reduction in the quantity of portlandite in the cement due to the consumption of Portlandite and generation of the secondary C-S-H. The amount of Ca $(OH)_2$ in the samples was also calculated from Eq (2). The test was performed on the samples cured for 24 hours at the pressure of 2200 PSI and the temperature of 50°C. The result obtained are given in Table 15.

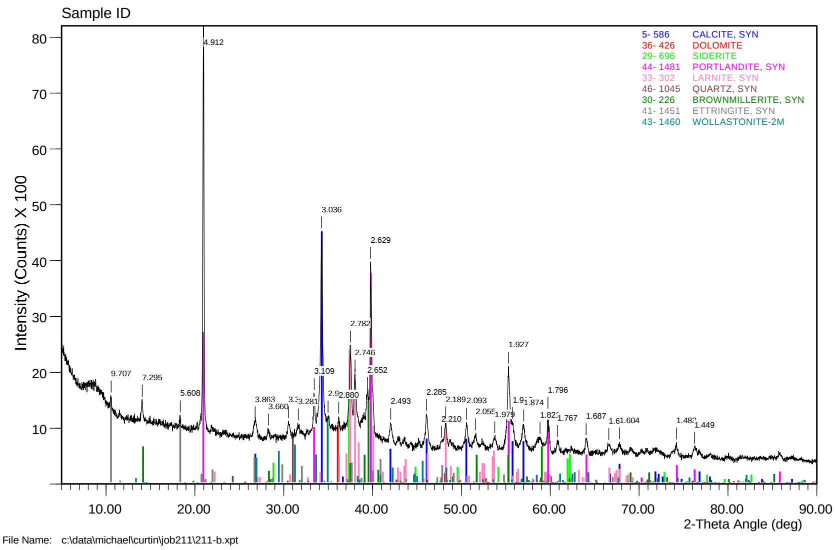
Table 15: The results obtained from performing TGA tests on 0.5 wt% NS and 5% POFA based cement

Cement Composite	Weight loss (%)	Percentage of Portlandite (%)
0.5% NS	2.36	9.7
5 % POFA	2.12	8.7

As it is seen in Table 15, a lesser amount of portlandite is left in the sample with POFA. However, the percentage difference between these two samples was only 10.9%. Considering the fact that only 0.5 wt% nanosilica was added to the cement, it seems that nanosilica is much active/reactive pozzolanic material than POFA.

4.5. XRD Analysis

Choosing two cement samples from each category as the best and representative samples, XRD analysis was only done on the 0.5 wt% nanosilica and 5 wt% POFA based cement. The samples selected were cured for 6 months under the ambient condition after one day of initial curing in the UCA. The XRD analysis was then performed and the RIR method was used for the calculation of the amount of portlandite left in the cement matrix. The results are shown in Figure 13 and Table 16.



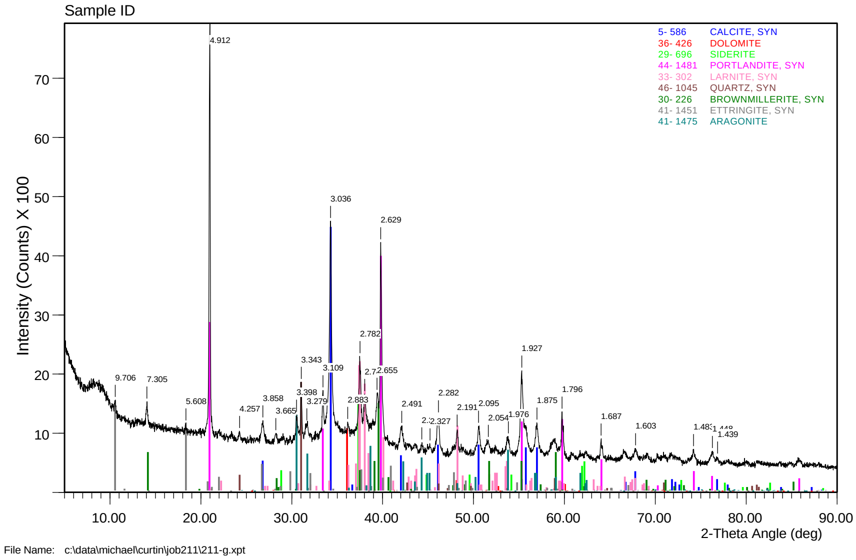


Figure 13: XRD analysis of 0.5 wt% nanosilica (top) and 5 wt% POFA (bottom) cement composites

Table 16: Amount of portlandite left in the samples after 6 months of curing

Cement composition	Portlandite (%)
Neat Cement	66
0.5% NS	50
5% POFA	43

From the result reported in Table 16, one can conclude that the least amount of Portlandite is present in the sample with 5 wt% POFA due to the continuous reaction of POFA with Portlandite long after the initial curing. That is the main reason why the highest compressive strength was produced by the 5 wt% POFA based cement after 9 months of curing.

4.6. SEM Analysis

SEM analysis was done to evaluate the structure of the nanosilica and POFA based cement after curing. It was also attempted to evaluate the effect of the dispersion method proposed by Abid et al. (2018) on the structure of the cement with nanosilica. Figure 14 shows the structure of POFA and nanosilica cement composites while Figure 15 compares the structure of the samples with 0.5 wt% nanosilica prepared by two different mixing techniques after 3 months of curing.

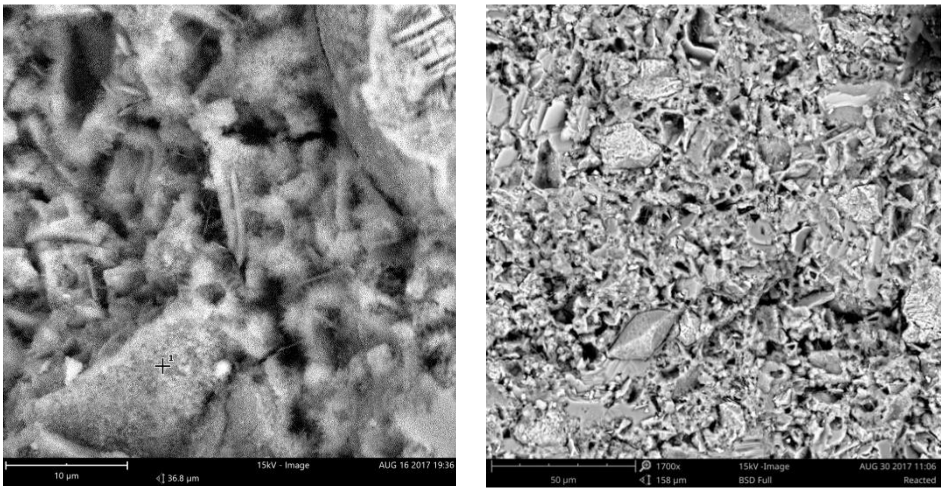


Figure 14: Structure of the cement samples with POFA (left) and nanosilica (right)

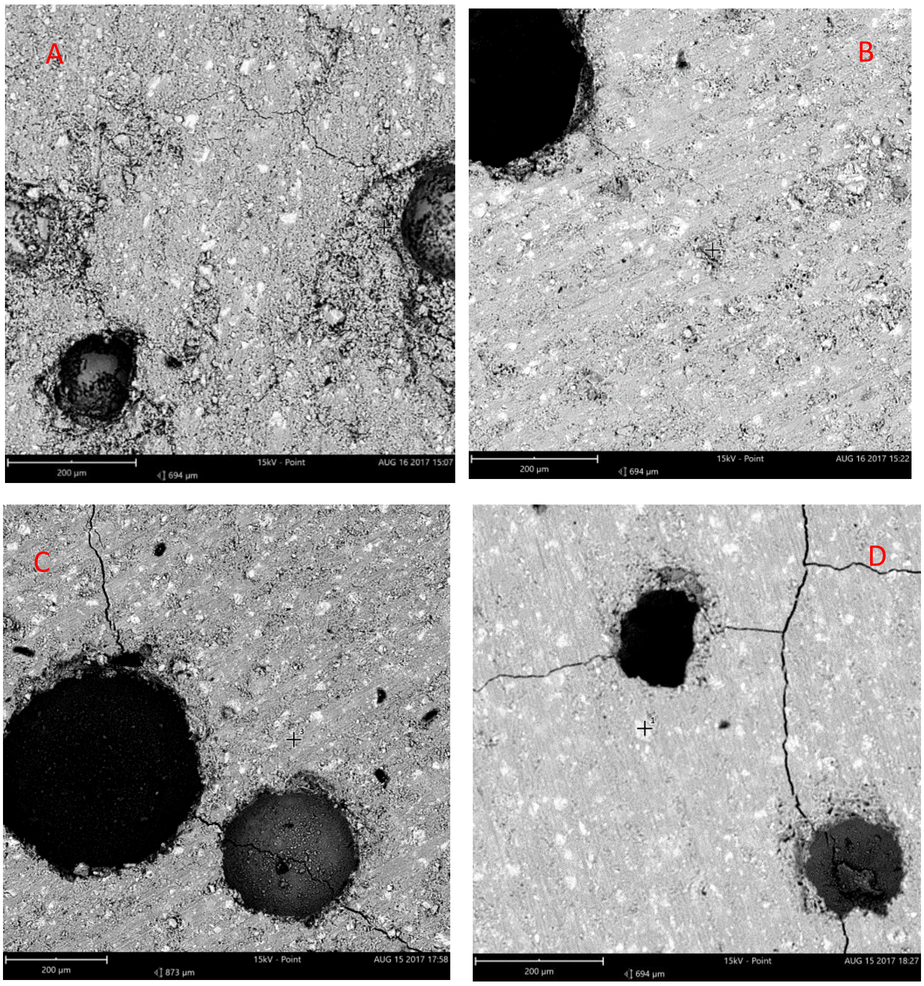


Figure 15: SEM analysis of the samples with 0.5 wt% nano silica after 3 months of curing. A) literature mixing cured in the water bath, B) new mixing cured in the water bath, C) literature mixing cured in the UCA and D) new mixing cured in the UCA

The results obtained indicated that the new mixing method recommended by Abid et. al (2018) gives a dense and smooth matrix to the cement compared to the conventional mixing method which is often reported in the literature. This could be due to the proper dispersion of nanosilica in the cement matrix which increases its reactivity with Portlandite. It was also appeared that the samples cured in the UCA have a very solid structure compared to the ones cured in the water bath. This highlights the effect of the pressure in the consolidation of the cement which should not be neglected.

5. Discussion

There have been many studies to improve the cement sheath integrity under different pressure and temperature conditions. It seems that the density of the cement with POFA remained the same as that of the neat cement whilst the plastic viscosity decreases as the quantity of POFA increases. In fact, although according to the free fluid test, POFA has a hydrophilic nature, unlike nanosilica and many other pozzolanic materials, it will not increase the viscosity and can be added by as much as 15 wt% without posing any drastic changes on the rheology of the cement slurry. This could be due to the fact that POFA acts as a filler and reduces the interlayer friction. Increasing the strength of the cement significantly and acting as a retarder are perhaps the best features of POFA which could not be observed in the cement mixed by nanosilica. However, POFA should only be added to the cement by a certain amount and its huge replacement can drastically affect the compressive strength development. In fact, according to the TGA, XRD and SEM analysis, the least amount of Portlandite and more densified structure was observed in the cement with only 5 wt% POFA. As a matter of fact, like many other Pozzolanic materials, POFA has a quantity threshold, which must not be exceeded when the cement is replaced for the strength enhancement. Considering the fact that the strength development in the cement continues months after placement, POFA, as a cheap additive which does not need dispersion for the cement preparation, could be a good option as a SCM in the oil well cementing industry.

6. Conclusion

In this study, the application of POFA, as an agricultural waste, in the oil well cementing was evaluated and compared with the nanosilica based cement through a series of tests recommended by the API. The results obtained revealed that POFA, as a cheap and largely available agricultural waste, not only gives a high strength to the cement in the early stage of the placement but also act as a retarder and strength development continues months after consolidation. Unlike many pozzolanic materials such as nanosilica, POFA will not disturb the rheology even in a high replacement and can even improve the workability if needed. Although there are certain precautions and procedures which must be taken in the lab to ensure that representative results are achieved, it seems that POFA based cement can be a great choice for the situations where a high strength development is required for maintaining the wellbore integrity.

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