Faculty of Engineering School

Designing a New Cement Composition Using Agricultural Wastes for Underground Gas Storage

Khizar Abid

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Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature: ……………………………………………

Date: 23rd August 2018

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Publications

- A review on cement degradation under CO_2-rich environment of sequestration projects, Journal of Natural Gas Science and Engineering, Volume 27, Part 2, November 2015, Pages 1149-1157
- A methodology to improve nanosilica based cements used in CO_2 sequestration sites, Petroleum, Volume 4, Issue 2, June 2018, Pages 198-208
- An Approach to Reinforce Class G Cement Using Agricultural Wastes: A Comparison Between the Performance of Wastes and Nano Materials (Revised for acceptance in Petroleum Science and Engineering Journal)
- Book Chapter as "Cement Degradation in CO_2 Geosequestration Sites. Mechanism, Interaction and Possible Solutions," in Petroleum Refining and Oil Well Drilling. Problems, Process and Industry Prospects, K. F. Olson, Ed., New York, Nove Science Publishers, 2017, pp. 127-160
- Book Chapter as "Chapter 27: Cement integrity in CO_2 sequestrations sites: An effective nano based approach" in Smart Nanoconcretes and Cement-Based Materials: Properties, Modelling and Applications, Nguyễn Tuấn Anh, Ed., Elsevier (Invitation received and writing has been started)

Abstract

Global warming posed by the release of greenhouse gases into the atmosphere is one of the biggest challenges attracting the attention of many researchers in the past decades. Carbon Capture and Sequestration (CCS) technology is one of the successful strategies used to capture CO_2 from different emission sites and inject it into suitable geological formations. It is, however, critical for CO_2 to remain confined without leaking into vital subsurface resources. One of the conventional problems observed in sequestration projects is degradation of Portland cement due to the exposure to supercritical (sc) CO_2 under the reservoir conditions. There have been many studies on the cement degradation under CO_2 rich environments, where it was indicated that the carbonation of cement is a self-healing process and degradation starts by the bi-carbonation of $CaCO_3$. It seems that adding certain amounts of pozzolanic materials may have a positive impact on the resistance of the cement but there is no indication as to how this amount should be calculated based on the water to cement ratio. The aim of this research is to use agricultural wastes based pozzolanic materials including Palm Oil Fuel Ash (POFA) and Rice Husk Ash (RHA) to develop a new class of cement which may resist the CO_2 attack. The agricultural wastes are relatively cheap and widely available in Malaysia and their applications have been shown in the civil industry successfully. Nano Silica (NS) was also used as part of the cement preparation to see the effect of nano particles on the overall performance of the cement. Before going through the carbonation test, a series of experiments were performed to evaluate the physical and mechanical properties of the cement, such as compressive strength (destructive and un-destructive), free fluid, density, and rheology. The cement samples were then exposed to $scCO_2$ for 40 days. At the end of the carbonation test, physical, morphological and mechanical properties of the samples were evaluated once again and changes were recorded for comparison purposes.

The results obtained indicated that the new mixing technique used to disperse Nano Silica (NS) into the cement matrix can help to ensure that the cement formulation gives a consistent result. The results also revealed that unlike the literature mixing, cement slurries prepared by the new mixing technique are very consistent in their rheology, regardless of the sonication parameters chosen. The measurements of the compressive strength performed at the reservoir condition revealed that nanosilica contributes to the strength development up to a certain point. Thermogravimetric Analysis (TGA) conducted at the last stage indicated that the amount of Portlandite left in the cement by adding nanosilica is decreased due to the pozzolanic reaction, which would help the cement to have a higher chance of survival in a storage site. However, caution must be taken to maintain a certain amount of Portlandite in the cement for slowing down the carbonation rate, as otherwise the matrix of the cement is attacked directly, and the cement will be degraded very fast. It was concluded that cement with 0.5 wt% nanosilica gives the best results in terms of physical and mechanical properties. A series of experiments were also conducted to evaluate 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. The density of the POFA based cement remained the same as that of the neat cement whilst the plastic viscosity gets lesser. After 24 hours and 9 months of curing, 5 wt% POFA based cement appeared to have the highest compressive strength which was further confirmed by their consolidated matrix observed through SEM and chemical analysis from XRD and TGA. A comparison of nanosilica with POFA based cement revealed that unlike POFA, nanosilica may significantly increase the plastic viscosity of the cement and cause difficulties during placement. It was also found that the compressive strength of POFA based cement is even higher than the nanosilica based cement after 9 months of curing. It was concluded that the POFA based cement can be a very good choice to improve the mechanical strength and matrix structure of the cement under different conditions.

Rice Husk Ash (RHA) was also considered as a supplementary cementing material (SCM) for this study. The results highlighted that the density of RHA based cement remains the same as that of the neat cement and as the quantity of RHA increases, the free fluid decreases and the plastic viscosity increases due to hydrophilic nature of RHA. Performing a series of destructive and non-destructive tests on the cement samples indicated that the cement can be replaced by as much as 3 wt% RHA. However, the WOC of all RHA cement composites was less than that of the neat cement.

In the last part of the thesis, those samples with the best performance from different categories were exposed to water saturated scCO_2 in the static reactor for 40 days. The temperature and the pressure of the static reactor was maintained above the critical point so that CO_2 can remain in the supercritical state. After the carbonation test, the phenolphthalein test was performed on all the samples and it was found that all of the cement composites have less carbonated area then the neat cement except the sample with 5 wt% POFA, although the least carbonated samples were those with 0.5 wt% and 0.75 wt% nanosilica. Upon carbonation, it was found that the compressive strength of the neat cement and nanosilica based cement increases which is typical in the carbonation process due to the self-healing process. However, agricultural waste-based cement showed a significant decrease in the compressive strength with the least strength provided by 5 wt% POFA. TGA analysis confirmed the results and indicated that a significant amount of Portlandite was left in the samples with 0.5 wt% nanosilica while the least was in the sample with 5 wt% POFA. Changes in the sample mass showed that 5 wt% POFA based cement has gone through the bi-carbonation stage. Overall, it was concluded that nanosilica based cement can be the best solution to resist the attack of $scCO_2$ if a proper dispersion method is employed. However, agricultural wastes can still be used in the places where the strength development of the cement is required at a cheap operating cost.

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Chapter 1: Introduction and Fundamentals

1.1 Introduction

The concept of Carbon Capture and Sequestration (CCS) was first introduced in 1977 when it was found that carbon dioxide (CO_2) emitted from the coal power plant could be captured and injected into suitable geological formations (Marchetti, 1977). The main objective of CCS is to reduce the amount of greenhouse gases released into the atmosphere and store them in subsurface geological sites for thousands of years. In this practice, CO_2 in a dry supercritical state[1] ($scCO_2$) is stored into depleted reservoirs, coal beds or saline aquifers (Bai et al., 2015; Barlet-Gouédard et al., 2009)

The success of CCS technology, however, depends mainly on three fundamental parameters known as capacity, injectivity, and confinement. Capacity of depleted reservoirs is generally defined as the amount of CO_2 which can be stored before fracturing the caprock. Capacity depends on numerous parameters including total organic carbon, thickness, effective porosity, permeability, CO_2 absorption isotherm and apparent gas saturation of reservoirs selected for storage purposes (Godec et al., 2013). However, there are limitations such as technical, economical, regulatory and physical issues, which restrain a full utilization of the storage capacity to its maximum theoretical limit (Bachu et al., 2007). Injectivity of a storage site, on the other hand, is defined to ensure that CO_2 can be injected at a desired rate. This rate can be improved by changing completion techniques, but often a reservoir has its own limit (Raza et al., 2015). The confinement is the last and probably the most important parameter that plays a significant role in the success of storage practices. The confinement must be evaluated at early stages since leakages of CO_2 contaminate fresh water resources and may have an adverse impact on vegetation, the environment, animals and people, when it reaches to the surface (Zhang and Bachu, 2011). This leakage comes not only from the

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[1] It corresponds to a state where the pressure and temperature of the medium can reach 7.38 MPa and 31.10°C respectively

fractured caprock but also occurs through the micro annulus flaws created due to the alteration or/degradation of the cement when exposed to $scCO_2$.

The most common types of cement used for sealing wells after CO_2 injections are Class G and H cement. Upon injection, $scCO_2$ dissolves into the formation water and produces CO_2-saturated formation water (carbonic acid) which chemically interact with Portlandite causing cement degradation (Bachu and Bennion, 2009; Carey, 2013). As a result of this degradation, $scCO_2$ is transported through the cement pore spaces while the rate of reaction is controlled by diffusion rate of the reactant. Hence, it is important to understand the chemical composition, hydration and kinetic reactions of the cement, and components susceptible to CO_2 attacks before and during injection. It is also imperative to discuss the possible effects of carbonation or/bicarbonation on the mechanical and transfer properties of the cement to ensure the long-term integrity of the storage sites.

1.2 Fundamentals of Cement Carbonation and Degradation

1.2.1 Chemical Composition of the Cement

As mentioned earlier, class G (Portland) cement is commonly used in the petroleum industry for sealing the injection sites in the wells chosen for a storage practice. This cement has a Blaine specific surface area of 280-340 m^2/kg (Kurdowski, 2014) and its compositions together with its functions are summarised Table 1-1.

Table 1-1: Compositions and specific functions of Class G cement (Adam and Charrier, 1985)

Compound	Cement Chemist Notation	Content (wt %)	Function
Tricalcium Silicate $(CaO)_3 . SiO_2$	C_3S	58	Enhances the strength and develops early strength
Dicalcium Silicate $(CaO)_2 . SiO_2$	C_2S	19	Hydrates slowly, Strength generated over time
Tricalcium Aluminate $(CaO)_3 . Al_2O_3$	C_3A	2	Promotes rapid hydration, affects thickening time and initial setting of the cement
Tetracalcium Aluminoferrite $(CaO)_4. Al_2O_3. Fe_2O_3$	C_3AF	11	Responsible for slow hydration

1.2.2 Hydration of Portland Cement

Portland cement is also known as the hydraulics cement since its strength is developed by the chemical reaction taking place between water and the cement. This process is called hydration and gives stiffness, solidification and hardening to the cement.

1.2.2.1 Hydration of Silicates

The most abundant phase in the Portland cement is silicate, comprising more than 80% of the cement (Nelson, 1990). Within this 80%, only 20% consists of C_2S while the concentration of C_3S may exceed 70%. The reaction of the silicate phase with water is given below (Mindess et al., 2003; Kosmatka et al., 2003; Mamlouk and Zaniewski, 2011)

$$2C_3S + 7H \rightarrow C_3S_2H_8 + 3CH \qquad (1\text{-}1)$$

$$2C_2S + 7H \rightarrow C_3S_2H_8 + CH \qquad (1\text{-}2)$$

In both of the above reactions, Calcium Silicate Hydrate (C-S-H) and Calcium Hydroxide (CH), which is also known as Portlandite, are produced. However, the amount of C-S-H produced by the C_3S is more than C_2S. The early strength in the cement is developed due to the hydration of the C_3S because the hydration rate of C_3S is much faster than that of C_2S. The strength contributed by C_2S, however, appears at the later stage of hydration (Kurtis, 2007). C-S-H is the main binding material in the cement and has a quasi-amorphous structure. In the hydrated cement, C-S-H occupies approximately 50-60% of the solid volume. The gluing characteristics of C-S-H is due to the covalent and/ionic bonding (~65%) and Van der Waals (~35%) bonding. Portlandite also has a definite stoichiometry and a crystalline structure with a variable morphology, ranging from thin elongated prism to large hexagonal prism shapes (Kurtis, 2007). In a fully hardened cement, the solid volume occupied by Portlandite is about 20 to 25%.

1.2.2.2 Hydration of Aluminate Phase

The hydration rate of C_3A is very rapid among the aluminate phases. The abundance of C_3A is much less than that of the silicate phase but has a greater impact on the rheology and early strength development of the cement. The hydration of C_4AF is similar to that of C_3A but at a much slower rate (Nelson, 1990). In the first step, C_3A reacts with gypsum (CSH_2) and water to yield ettringite ($C_6AS_3H_{32}$) as below:

$$C_3A + 3CSH_2 + 26H \rightarrow C_6AS_3H_{32} \qquad (1\text{-}3)$$

The stability of the ettringite is dependent on the availability of gypsum. It is worth mentioning that the ettringite does not contribute to the strength development of the cement. Once all the gypsum is consumed, the ettringite starts to react with any remaining C_3A to form monosulphate aluminate hydrate crystals which is expressed as:

$$2C_3A + C_6AS_3H_{32} + 22H \rightarrow 3C_4ASH_{18} \qquad (1\text{-}4)$$

The monosulphate crystals are stable in the sulphate deficient solution. These monosulphate crystals, however, may bounce back again to the ettringite in the presence of sulphate. The size of the ettringite crystal is two and a half times bigger than the monosulphate crystal and is responsible for the cracking of the cement in the presence of sulphate (Mindess et al., 2003; Kosmatka et al., 2003; Mamlouk and Zaniewski, 2011)

1.3 Supercritical Carbon Di-oxide ($scCO_2$)

Supercritical state is referred to the state of CO_2 where the temperature and pressure exceeds the critical point. Under the supercritical state, CO_2 exhibits a liquid like density but a gas like viscosity. Diffusivity, however, will be something between gas and liquid. The critical pressure and temperature for CO_2 is 31°C and 1070PSI (74Bar) respectively (Peach and Eastoe, 2014). When CO_2 is pumped in the subsurface layers for the storage purpose, the temperature and pressure of the subsurface will push it into the supercritical state. Therefore, the reactivity and diffusivity of $scCO_2$ will be faster than that of CO_2 in any other phases. The phase diagram of $scCO_2$ is shown in Figure 1-1.

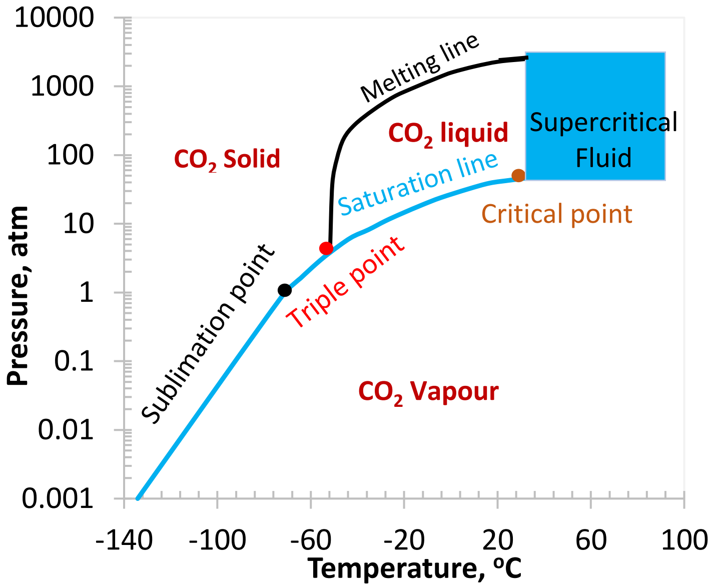

Figure 1-1: Pressure-Temperature phase diagram of carbon dioxide

1.4 Carbonation and Bi-Carbonation of Portland Cement

The attack of CO_2 to the cement is initiated by the carbonation of Portlandite ($Ca(OH)_2$). Once Portlandite is consumed, the C-S-H phase is decomposed into $CaCO_3$ and silica gel, resulting in a considerable reduction of the cement's strength. Although it was shown in few studies that the decomposition of C-S-H is concurrent with that of the Portlandite, it is certain that carbonation leads to bi-carbonation, which in turn leads to the degradation of the cement (Kutchko et al., 2007). This degradation can be expressed by the following chemical reactions (Kutchko et al., 2007) as demonstarted in Figure 1-2.

$$CO_{2\,(aq)} + H_2O \rightarrow H_2CO_{3\,(aq)} \tag{1-5}$$

The carbonic acid diffuses in the cement, causing dissociations of Portlandite as below:

$$Ca(OH)_{2\,(s)} \rightarrow Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)} \tag{1-6}$$

This degradation is followed by:

$$Ca^{2+}_{(aq)} + HCO_3^{-}{}_{(aq)} + OH^{-}_{(aq)} \rightarrow CaCO_{3(s)} + H_2O \tag{1-7}$$

As a result, a polymorph of $CaCO_3$ is formed and carbonated water diffuses towards the cement sheath. This is known as carbonation in which a self-healing process takes place, porosity and permeability decreases, and mechanical properties (i.e., compressive and tensile strength) of the cement increases (Nygaard, 2010). As diffusion continues, abundance of HCO_3^- leads to the formation of calcium bicarbonate, which is soluble in water and can be leached out of the cement matrix. This step is also known as bi-carbonation and is expressed by using the following reaction:

$$H^{+}_{(aq)} + CaCO_{3\,(s)} \rightarrow Ca^{2+}_{(aq)} + HCO_3^{-}{}_{(aq)} \tag{1-8}$$

At the end of bi-carbonation, a complete degradation of the cement is observed where C-S-H reacts with H_2CO_3 to form $CaCO_3$ together with amorphous silica gel, as addressed below:

$$3\ H_2CO_3 + Ca_3Si_2O_7 * 4H_2O \rightarrow 3\ CaCO_3 + 2\ SiO_2 * H_2O + 5\ H_2O \tag{1-9}$$

This last stage of degradation is characterized by an increase in porosity and permeability, as well as reduction of the mechanical strength of the cement. The increase in permeability and porosity is linked to the fact that the molar volume of C-S-H is larger than that of $CaCO_3$ produced during the degradation (Nygaard, 2010). On the other hand, the release of the amorphous silica gel from the cement matrix is the reason why the mechanical strength of the cement decreases (Kutchko et al., 2007).

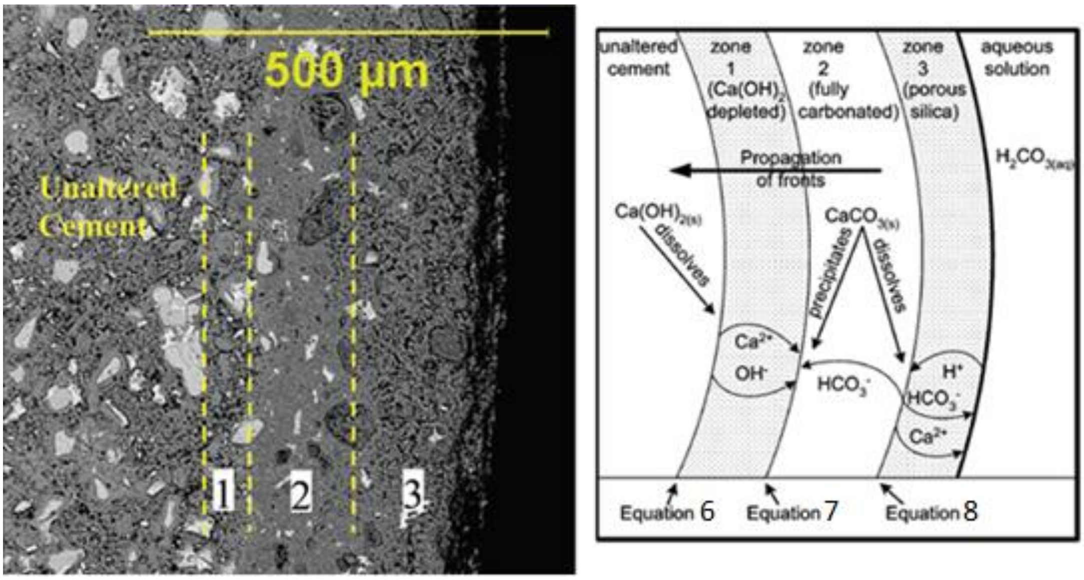

Figure 1-2: A SEM-BSE image (left) and a schematic diagram (right) showing the carbonation propagation front of Portland cement (Kutchko et al., 2007)

1.5 Research Gap

The literature review revealed that a certain quantity of pozzolanic materials improve the resistance of the cement exposed to supercritical CO_2, but there is no indication as to how this amount should be selected. Moreover, it seems that more studies are required to clarify the application of pozzolanic materials when they are added to the well cement used for sealing of the CO_2 storage sites. Thus, in this study, cheap pozzolanic materials such as Palm Oil Fuel Ash (POFA) and Rice Husk Ash (RHA) together with nano materials such as Nano Silica are used to formulate a cement composition which can provide resistance against the attack of dry/wet CO_2 in a storage site.

1.6 Aim and Objectives

The aim of this research is to formulate a new cement composition using agricultural waste, such as Palm Oil Fuel Ash (POFA) and Rice Husk Ash (RHA), either with or without nano particles, which can maintain its mechanical and other essential physical properties in a CO_2 rich environment.

The objectives of this research are:

i. To propose a proper dispersion technique of nano particle in the cement.
ii. To determine the optimum quantity of pozzolanic to cement ratios that gives the best physical and mechanical properties.
iii. To evaluate the carbonation front and degradation of the cement composite by exposing the samples to reservoir conditions in the presence of $scCO_2$.
iv. To propose the best cement composition which can provide a good resistance against supercritical (sc) CO_2.

1.7 Significance

Considering the fact that depleted formations chosen as the storage sites should be able to hold CO_2 for thousands of years, it would be crucial to ensure that the cement type used to seal the injection sites can maintain its integrity during and after exposure to $scCO_2$. Many discussions have been made as to how cement properties should be improved without increasing the cost of cement production. This study attempts to develop a cheap cement composition which can be used to ensure the long-term integrity of cement systems targeted for CO_2 storage sites.

1.8 Scope

Objective 1

- Dispersion of Nano Silica in the cement matrix and monitoring the changes in the rheological properties.
- Evaluating the improvement of the mechanical, chemical and morphological properties of the dispersed Nano Silica cement composite.

Objective 2

- Evaluating the rheological properties and free fluid of conventional Portland cement samples as per API standard.
- Evaluating the mechanical properties of the cement samples in terms of compressive strengths under destructive and non-destructive conditions.
- Measurement of the chemical composition of the samples by Thermo Gravimetric Analysis (TGA) and XRD.

- Analysis of the cement matrix through SEM.

Objective 3

- Placing the best cement prepared by agriculture wastes and nano particles in the static reactor under CO_2 storage conditions.

Objective 4

- Measuring the physical, chemical and mechanical properties of the samples surviving the carbonation through phenolphthalein test, compression test, TGA, mass measurement and microscopic image analysis.

Chapter 2: Literature Review

2.1 Introduction

In this chapter laboratory experiments performed by different authors on the cement carbonation and bicarbonation are discussed. It is evident from these studies that the carbonation of the well cement is a self-healing process. However, as the ingression of $scCO_2$ continues, bicarbonation takes place, leading to the degradation of the cement. Therefore, several approaches to resist the attack of CO_2 have been formulated where addition of pozzolanic materials in the cement found to be the best approach to enhance the resistance against the carbonation.

Pozzolanic materials discussed in the chapter are agricultural wastes known as Palm Oil Fuel Ash (POFA) and Rice Husk Ash (RHA). They have shown applications in the civil industry where reinforcement of the cement matrix was reported. Nano particles such as Nano Silica (NS) can also provide pozzolanic reactions and may be a good choice to be added to the cement for a better performance in the storage sites. However, the optimum quantity of the pozzolanic material in the well cement has not been fully understood and further studies are still required to get a conclusion as to how pozzolanic materials can provide the best performance upon mixing by the cement.

2.2 Background

2.2.1 Neat Cement[1] Degradation

Many laboratory experiments have been carried out to understand the behaviour of the cement in a CO_2 rich environment. These experiments are usually carried out in a High Pressure High Temperature (HPHT) vessel (Figure 2-1) in order to simulate the reservoir conditions. The vessel comprises of two parts: the bottom half contains a brine solution so that $scCO_2$[2] can be dissolved to give brine saturated CO_2 while the upper half contains $scCO_2$, known as the wet $scCO_2$ (Barlet-Gouédard et al., 2009).

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[1] Neat cement is defined as the sample consist mainly of pure cement without any additives.

[2] $scCO_2$ is the state of fluid which exists at a temperature and the pressure of above 31.10°C and 73 Bars respectively.

Using this apparatus, the effect of the curing, additives, water to cement ratio and water salinity on the cement carbonation is examined. The time period of the carbonation test is typically from one month to one year, during which cement samples are monitored constantly to evaluate the depth of carbonation. Tests are carried out in both dynamic (i.e., a certain flow rate of brine/water is maintained in the pressure vessel) and static (brine/water remains in the static state having no flow rates) conditions, but it is recommended to run the test under static conditions for more representative results (Kutchko et al., 2007). Although there have been many studies on the cement degradation, only few of them provided promising results.

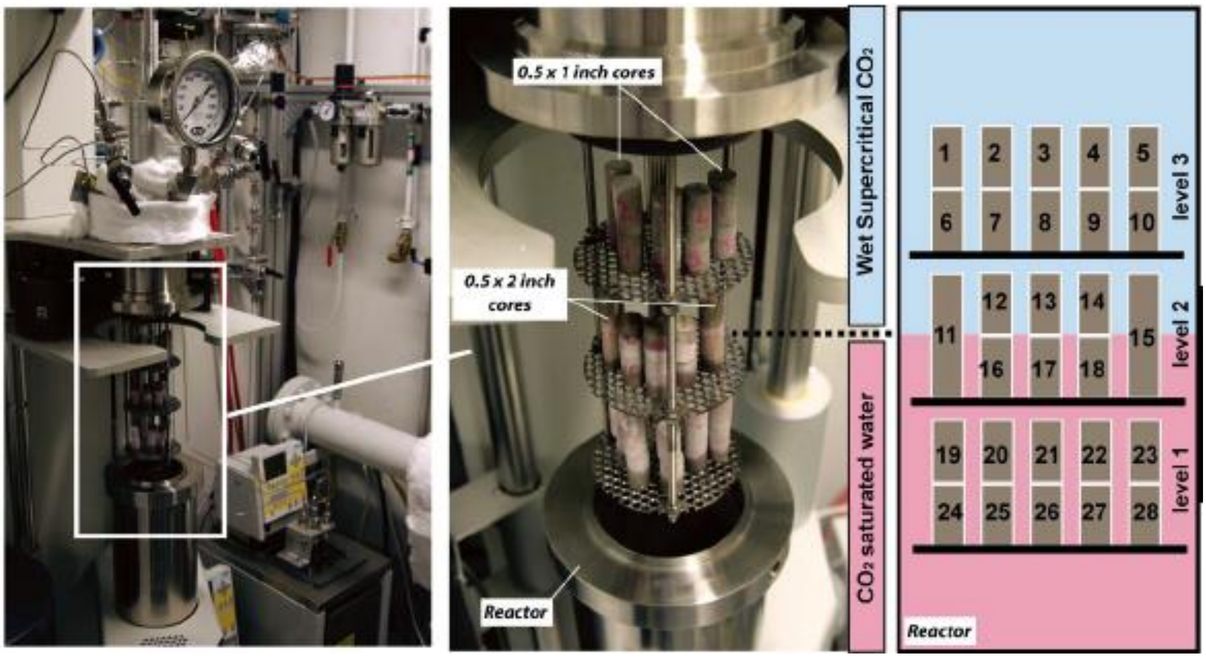


Figure 2-1: Pressure vessel used to examine degradation of neat cement (Barlet-Gouedard et al., 2009)

For instance, a series of tests were performed by Duguid et al. (2004, 2005) and Duguid and Scherer (2010) on the well cement exposed to $scCO_2$. The dynamic test condition was used for the purpose of the tests and pH of the leaching solution (CO_2 saturated brine) was kept between 2.4 and 3.7 at the temperature of 50°C and 20°C respectively. Duguid et al. (2004) used two sets of samples: one set consisted mainly of the neat Class H cement while the other comprised of cement with 6% bentonite. The carbonation test was performed for 1-7 days and it was reported that the porosity of the neat cement can be increased to as much as 45% in a CO_2 rich environment. It was also discovered that the rate of reaction in the samples containing bentonite was higher than that of the neat cement. Duguid et al. (2005) exposed the neat cement to $scCO_2$ for 31 days. Although the tests were carried out at two different temperatures of 50°C and 20°C and pH of 2.4 and 3.7, the highest rate of reaction was observed at 50°C and pH of 2.4. Duguid and Scherer (2010) did a series of similar studies in which the effect of pH was recorded for 26 days. They did not observe any degradations in the samples exposed to $scCO_2$ with a leaching solution of pH 5 and concluded that if $CaCO_3$ can be dissolved in the formation water, pH increases and degradation stops. Therefore, sandstone reservoirs which cannot provide any dissolution of $CaCO_3$ in the formation water are often considered as a harsh environment for well cementing. It should be noted that the above experiments were run under the dynamic conditions and may not be a true representative of the reservoir conditions.

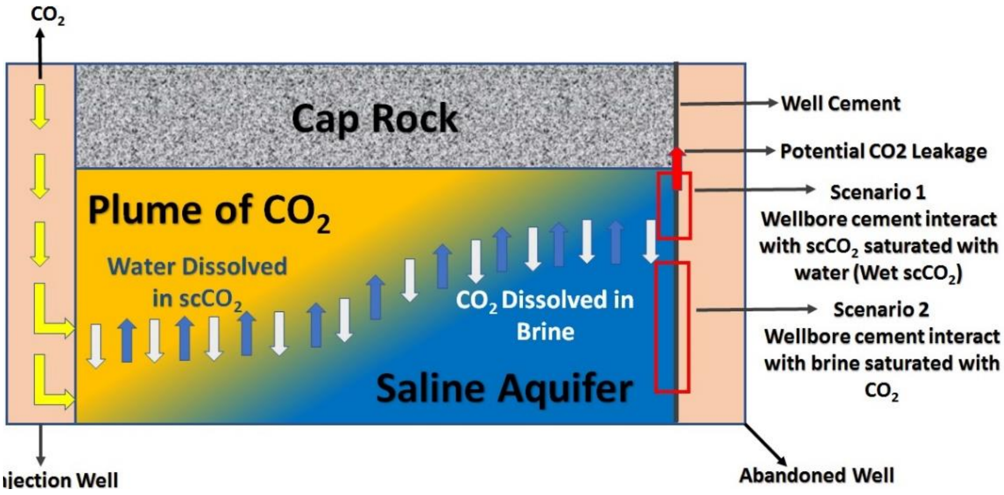


Figure 2-2: Reservoir condition showing interaction of $scCO_2$ with the cement

Kutchko et al. (2007, 2008) carried out a series of experiments in which neat class H cement samples were exposed to $scCO_2$ under the reservoir conditions. The samples were placed in a HPHT vessel and static condition was applied for the carbonation test. The pressure of $scCO_2$ was 30.3 MPa and the temperature was increased to as much as 50°C. Kutchko et al. (2007) evaluated the impact of the curing condition on the cement carbonation by curing the samples at different temperature and pressure conditions for 28 days. They observed the least carbonation in the samples cured at 30.3 MPa and 50°C. This study was further investigated by Kutchko et al. (2008) where the carbonation test was carried out for a year. They concluded that the carbonation reaction is controlled by diffusion for samples exposed to $scCO_2$. The carbonation propagation front, on the other hand, was quite complex for the samples exposed to CO_2 saturated brine.

Barlet-Gouedard et al. (2006, 2007) stated that the flow of formation fluids in reservoir conditions is following a static, not a dynamic condition. They performed a series of experiments on the well cement under a static condition where the temperature and the pressure of the vessel was kept at 90°C and 28 MPa, respectively, for up to 6 months. A rapid increase in the density was observed within 4 days of exposure but it was stabilized afterwards. After 6 weeks of exposure, a large drop in the compressive strength was observed for the samples located in the CO_2 saturated water. Although permeability remained below 8md even after the exposure, porosity increased in the samples located at the top or bottom of the vessel. In fact, porosity decreased when $CaCO_3$ was formed during the carbonation of the cement but increased when $CaCO_3$ was transformed into $Ca(HCO_3)_2$ and leached out of the cement. This leaching was, however, faster in the presence of CO_2 saturated water than $scCO_2$. Barlet-Gouedard et al. (2009) indicated that the formation fluid consists mainly of brine and it should be used for the carbonation test rather than fresh water. They performed similar experiments conducted by Barlet-Gouedard et al. (2006, 2007) and used a 0.4M NaCl brine solution instead of fresh water. They observed a dramatic fall in the propagation rate of the samples after two days of exposure to CO_2 saturated brine. This decrease in the alteration rate was due to the fact that the concentration of CO_2 dissolved in brine was less than that of the CO_2 in fresh water.

Costa et al. (2017) did a series of experiments to evaluate the effect of carbonation based on the sedimentation on the class G cement. The samples were exposed to the fresh water saturated $scCO_2$ at the temperature of 70°C and pressure of 2000PSI for 30 days. The results showed that the stable sedimentation formulation of the cement gave the uniform distribution of the carbonation profile whereas unstable sedimentation in the cement gave non-homogenous profile of the carbonation. In their second set of experiment, Costa et al. (2018) recorded the effect of the carbonation on the curing age. In this study, samples of class G cement were cured for 8 hours, 7 days and 28 days after which the samples were exposed to $scCO_2$. A similar set of tests were conducted on the cement and after30 days of exposure, it was observed that changes in the density of the samples after carbonation are close to each other regardless of the curing period. It also appeared that the sample cured for 7 days has gone through more carbonation because the hydrated product was not enough to restrict the ingression of $scCO_2$. However, a resistant behaviour of carbonation was observed in the samples cured for 8 hours and 28 days which could be due to the fact that the samples with 8 hours have not produced enough hydrated products that will react with $scCO_2$. On the other hand, 28 days cured cement samples have already produced enough hydrated products that will reduce the permeability and porosity in the cement matrix to restrict the propagation of $scCO_2$.

The experimental investigations performed so far on the neat cement confirmed that degradation is taking place under CO_2 rich environments. Thus, numerous attempts were made to propose a solution to either mitigate or prevent this degradation. In the next section, recent studies carried out to design a cement formulation for CO_2 sequestration projects are reviewed and their drawbacks are reported.

2.3 Developed Approaches to Resist the $scCO_2$ Attack

Some of the approaches developed so far to resist the attack of CO_2 are presented in this section together with their limitations. These methods are categorized into 4 groups as below:

I. **Pozzolanic Materials:** These materials can reduce the permeability and quantity of the Portlandite when they are added to the cement. A pozzolanic material is mainly composed of SiO_2 (and Al_2O_3), which reacts with Portlandite to give secondary C-S-H. The SiO_2 further reduces the water content of the cement and decreases the Ca/Si ratio creating a longer chain of C-S-H (high silicate polymerization), which increases the strength of the cement. As the permeability of the cement decreases, ingression of CO_3^- is hindered and carbonation is avoided (Ilesanmi, 2013; Bai et al., 2015). This pozzolanic reaction is addressed as shown below (Brandl et al., 2011)

$$Ca(OH)_2 + SiO_2\ (Al_2O_3) \rightarrow \text{C-S-H (C-A-S-H) phases} \tag{2-1}$$

II. **Water to Cement Ratio:** As the water to cement ratio decreases, the un-hydrated cement clinker increases, causing the permeability of the cement to reduce and the density to increase (Barlet-Gouedard et al., 2012). This density increase, however, may result in raising the possibilities of fractures in soft formations.

III. **Non-Portland Cement:** These cements are not generally recommended because of its high cost and low availability (Benge, 2009)

IV. **Epoxy Resins:** These resins are able to chemically coat the cement and resist the attack of CO_2. They are, however, degraded rapidly under a CO_2 rich environment when tested at 90°C and 28MPa for 31 days (Barlet-Gouedard et al., 2012).

2.4 Experimental Investigations

Among the approaches presented so far, applications of pozzolanic materials in enhancing the cement resistance have gained a lot of attention in recent years. For instance, Santra et al. (2009) performed a series of experimental investigations where different quantities of silica fumes and fly ash were mixed with the cement. The carbonation test was carried out at 93°C and 14MPa for 15 to 90 days in CO_2 saturated water. The results showed that although the rate of penetration of CO_2 was higher in the cement with pozzolanic materials, the carbonation of $Ca(OH)_2$ or C-S-H was less than that of the neat cement due to the absence of $Ca(OH)_2$ in the samples. It was concluded that as the amount of pozzolanic material increases, the ability of the cement to survive in a CO_2 rich environment improves.

Brandl et al. (2011) carried out a series of experiments to compare the conventional oil well cement with the one having pozzolanic material included in its composition. They did a degradation test in a HPHT vessel at the temperature of 149°C and the pressure of 20.6 MPa over a period of six months. The results obtained indicated that pozzolanic samples, after 6 months of reaction, have not yet gone through full carbonation, but the conventional samples were completely carbonated. They concluded that a certain amount of pozzolanic materials enhances the resistance to CO_2 exposure while, in contrast, an excessive amount of pozzolanic material may have a negative impact.

Garnier et al. (2010) reported experiments with two sets of samples. One was neat Class G cement tested at a temperature of 90°C and a pressure of 8MPa for 90 days whilst the second sample consisted of the class G cement with silica flour (35% By Weight of Cement (BWOC)). The second sample was exposed to the pressure of 8 MPa at the temperature of 140°C for 88 days. The test was carried out under the static condition and it was found that the rate of alteration for the second sample was remarkably less than that of the neat sample.

Lesti et al. (2013) reported a series of experiments on different types of cement to evaluate the effect of adding pozzolanic materials. They prepared samples consisting of 1) inorganic material + cement, 2) slag cement + fly Ash, 3) organic latex particles + cement and 4) neat class G cement. These samples were placed in an autoclave/pressure vessel while the temperature and the pressure of injected $scCO_2$ were kept at 90°C and 40MPa respectively, for 6 months. They pointed out that the best results, in terms of mechanical and transfer properties, were obtained by sample No. 2 due to the pozzolanic reaction of Fly Ash with Portlandite.A

Zhang and Talman (2014) carried out experimental investigations on three different samples consisting of neat class G cement, pozzolanic cement (fly ash with 2% of bentonite) and light weight sample (fly ash with 1% of sodium metasilicate). The experiment was performed at the temperature and the pressure of 53°C and 10MPa in the presence of a 0.5M NaCl solution for 84 days. The obtained results revealed that although the pozzolanic mix sample was fully carbonated but its durability and permeability remained unchanged. The Lightweight cement, on the other hand, totally lost its durability and permeability after 84 days of reaction. Hence, it was postulated that the cement containing pozzolanic material might be a good choice for a CO_2 rich environment.

Following the recommendation of Zhang and Talman (2014), Zhang et al. (2014) evaluated the effect of pozzolanic materials on the cement resistance. Two cement samples of class H with different quantity of fly ash were tested. Samples were exposed to $scCO_2$ at the temperature and the pressure of 50°C and 15MPa respectively for 28 days. They concluded that samples with a small amount of pozzolan gives a better performance than those having a high pozzolan to cement ratio. Zhang et al. (2014) reached a very same conclusion indicating that a lower pozzolan to cement ratio enhances the cement resistance against $scCO_2$. However, they did not indicate how this amount should be selected.

Aiex et al. (2015) compared the performance of 100% Portland cement (Class G) to a 100% cement blend exposed to $scCO_2$. The experiment was held in a $scCO_2$ environment for 12 months. After exposure, it was recommended that fresh water would be a better choice than brine for mixing cement. It was also concluded that a certain amount of cement should be replaced either by blast furnace slag or pozzolanic materials in order to have a better performance in a CO_2 rich environment. Table 2-1 provides a review on recent studies carried out on the cement degradation in a CO_2 rich environment.

Table 2-1: A summary of experimental investigations and findings reported in recent studies

Authors	Preparation of the sample	Ratios of Pozzolan/water	Curing Condition	Experimental setup	Finding
Duguid et al. (2004)	• Two samples used: (1) Class H cement + DI water (2) Class H cement + 6% Bentonite + DI water • Size (Dia*H) = 7.3-7.7mm*140-260mm	• Water to solid ratio: (1) 0.38 (2) 0.70	• Cured in 0.5M NaCl • Room Temperature • 28 Days	• CO_2 saturated brine with different pH i.e. 3.7 and 2.4 • Exposure Time = 1.3 to 7.2 days • Temperature = 23°C and 50° Condition = Dynamic	• Rate of reaction for sample containing bentonite was high as compared to the neat cement • Sealing properties of the cement can be compromised even with the short term exposure of cement with carbonated brine
Duguid et al. (2005)	• One sample used: (1) Class H cement • Size (Dia*H) = 7.5mm*200mm	• Water to solid ratio: (1) 0.38	• Cured in 0.5M NaCl • Temperature = 20 and 50°C • 12 months	• CO_2 saturated brine with different pH i.e. 3.7 and 2.4 • Exposure Time = 31 days • Temperature = 23°C and 50°C • Condition = Dynamic	• Highest rate of reaction for the neat sample was observed at 50°C and pH of 2.4 to be about 0.07 and 0.24 mm/day • Lower the pH greater will be the rate of carbonation
Barlet-Gouedard et al. (2006,2007)	• Portland Cement + conventional additives • Size (Dia*H) = 12.7mm*25.4mm and 25.4mm*50.8mm	N/A	• Cured for 72 Hours • Temperature 90°C • Pressure 28 MPa	• Wet $scCO_2$ • CO_2 saturated water • Exposure Time = Days (0.5, 2, 4, 7, 21, 42) & Months (3 and 6) •Temperature = 90°C • Pressure = 28 MPa • Condition = Static	• The rate of reaction or alteration rate was diffusion controlled and was calculated to be $L = 0.26*t^{1/2}$ for the CO_2 saturated water and $L = 0.22*t^{1/2}$ for wet $scCO_2$ (whereas L is in mm and t is in hours) • Cement is more vulnerable to CO_2 saturated water than $scCO_2$

Authors	Preparation of the sample	Ratios of Pozzolan/water	Curing Condition	Experimental setup	Finding
Kutchko et al. (2007)	• Class H cement • Size (Dia*H) = 12mm*130mm	• Water to cement ratio (1) 0.38	• Cured in 1% of NaCl • Under different temperature and pressure: (1) 22°C and 0.1 MPa (2) 22°C and 30.3 MPa (3) 50°C and 0.1 MPa (4) 50°C and 30.3 MPa • 28 Days	• Wet $scCO_2$ • CO_2 saturated brine •Exposure Time = 9 days •Temperature = 50°C • Pressure = 30.3 MPa • Condition = Static	• After 9 days of exposure the depth of carbonation for all the samples were less than 1mm while lowest carbonation depth was observed in the cement sample cured under 50°C and 30.3 MPa
Kutchko et al. (2008)	• Class H cement • Size (Dia*H) = 12mm*130mm	• Water to cement ratio (1) 0.38	• Cured in 1% of NaCl • Temperature = 50°C • Pressure = 30.3 MPa • 28 Days	• Wet $scCO_2$ • CO_2 saturated brine • Exposure Time = up to 12 months • Temperature = 50°C • Pressure = 30.3 MPa • Condition = Static	• Sample present in $scCO_2$, reaction was diffusion controlled and the depth of carbonation was given as $L = 0.016*t^{1\backslash 2}$ (L is in mm and t is in days) • Sample exposed to CO_2 saturated brine, carbonation propagation was complex and an empirical formula was developed to estimate the depth of carbonation i.e. $L = 0.09\ln(t) + 0.17$
Barlet-Gouedard et al. (2009)	• Portland Cement + conventional additive • Size (Dia*H) = 12.7mm*25.4mm and 25.4mm*50.8mm	N/A	• Cured for 72 Hours • Temperature = 90°C • Pressure = 20.68 MPa	• Wet $scCO_2$ • CO_2 saturated brine • Exposure Time = 2 days • Temperature = 90°C • Pressure = 20.68 MPa • Condition = Static	• Decrease in the propagation\alteration rate was observed after two days of exposure of cement to CO_2 saturated brine as compared to CO_2 saturated in fresh water (200µm against 2mm)

Authors	Preparation of the sample	Ratios of Pozzolan/water	Curing Condition	Experimental setup	Finding
Brandl et al. (2010)	• Two sample used: (1) Class G cement + Silica Flour + (Chemically inert) Pozzolan (2) Class G cement + 35% BWOC Silica Flour • Size (Dia*H) = 25.4mm*50.8mm	• Water to solid ratio (1) 0.55 (2) 0.72	• Cured for 4 days • Temperature = 149^{o}C • Pressure = 20.68 MPa	• CO_2 saturated water • Exposure Time = 1, 3 and 6 months • Temperature = 149^{o}C • Pressure = 20.68 MPa • Condition = Static	• After the test it was observed that for all the samples, permeability was lower than 0.01mD and the compressive strength was greater than 5,000 Psi • Sample 1 gave better results w.r.t mechanical properties and durability
Garnier et al. (2010)	• Two samples used: (1) Neat class G cement (2) Class G + Silica Flour • Size (Dia*H) = 20mm*40mm	• Silica flour added 40% BWOC	Cured at different condition: • First sample: Pressure = Atmospheric Temperature = 90^{o}C 28 Days • Second Sample: For first 10 days: Pressure = 20.7 MPa Temperature = 140^{o}C For rest 18 days: Pressure = Atmospheric Temperature = 90^{o}C	• For both samples: CO_2 saturated water Pressure = 8 MPa Condition = static • First Sample: Exposure time = 7, 36, 65 and 90 days Temperature = 90^{o}C • Second Sample: Exposure time = 4, 12, 21, 31, 55, 88 days Temperature = 140^{o}C	• For sample 1 the rate of alteration was 4mm after 65 days of exposure and was diffusion controlled (linear to the square root of time) • For sample 2, progression of the carbonation front was 0.2 mm/day corresponding to 88 days of test, controlled by the reaction kinetic (carbonation front advances linearly with time).
Duguid and Scherer (2010)	• Two samples used: (1) Class H cement + DI water, (2) Class H cement + 6% Bentonite + DI water • Size (Dia*H) = 7.5mm*200mm	• Water to solid ratio (1) 0.38 (2) 0.70	• Cured in 0.5M NaCl • Temperature = 20 or 50^{o}C • 12 months	• CO_2 saturated brine with different pH i.e. 3.7, 2.4 and 5 • Temperature = 50^{o}C • Exposure Time: 26 Days • Condition: Dynamic	• No carbonation was reported in the sample present in pH 5 effluent

Authors	**Preparation of the sample**	**Ratios of Pozzolan/water**	**Curing Condition**	**Experimental setup**	**Finding**
Duguid et al. (2011)	• Two sample used: (1 and 2) Class H cement casted in hole of 25mm Dia of sandstone and limestone cylinder 55mm in height	• Water to cement ratio (1 and 2) 0.38	• Cured in 0.5M NaCl • Temperature = 20 or 50^{o}C • 7 months	• CO_2 saturated brine with different pH i.e. from 3 to 7 • Temperature = 50^{o}C • Exposure Time: 1, 2, 3, 6 and 12 months • Condition: Dynamic	• Sever condition for the degradation of the cement exist in the sandstone reservoirs environment as compared to the limestone or dolomite formation
Barlet-Gouedard et al. (2012)	Two sample prepared: • Portland cement + Silica + Metakaolin + Hollow Micro sphere • Slag cement + Micro Silica + Coarse particle + Hollow Micro sphere	• Blend Composition: Cement 100% + Silica 35% + Metakaolin 48.58% + Hollow microsphere 32.90% + Fresh Water • Blend composition: Slag Cement 100% + Micro Silica 28.76 + Coarse particle 180.81/72.32% + Hollow sphere 9.96/33.86%	• Cured for 3 days at 90^{o}C	• Wet $scCO_2$ • CO_2 saturated water • Exposure Time = 31 days • Temperature = 90^{o}C • Pressure = 28 MPa • Condition = Static	• Both cement composition performed well under CO_2 rich environment in the laboratory as compared to the neat cement and can be used with variety of densities
Lesti et al. (2013)	• Four samples prepared: (1) Inorganic material + Cement (2) Slag cement + Fly Ash (3) Organic latex particle + Cement (4) Neat Class G cement • Size (Dia*H) = 30mm*50mm	• Water to solid ratio: (1) 0.25 (2) 0.37 (3) 0.33 (4) 0.43 • Quantity added of additives can be seen from Lesti et al., (2013)	• Cured in synthetic reservoir fluid • Pressure 40 MPa • Temperature 90^{o}C • 28 Days	• Wet $scCO_2$ • CO_2 saturated synthetic reservoir fluid • Exposure Time = 1 and 6 months • Temperature = 90^{o}C • Pressure = 40 MPa • Condition = Static	• Main phenomena in the degradation of the cement is due to the crystallization of $CaCO_3$ that result in the cracking of cement matrix. • Sample 2 gave the best result w.r.t to the durability because less quantity of $CaCO_3$ formed

Authors	**Preparation of the sample**	**Ratios of Pozzolan/water**	**Curing Condition**	**Experimental setup**	**Finding**
Zhang et al. (2014)	• Two samples were prepared with different quantity of Fly Ash: (1 and 2) Class H Cement + Fly ash (F) • Size (Dia*H) = 12mm*60mm	• Ratio by volume of poz to cement: (1) 35:65, w/s (0.51) (2) 65:35, w/s (0.56)	• Cured in 1% NaCl • Pressure = 15 MPa • Temperature = 50°C • Days 28	• Wet $scCO_2$ and H_2S • CO_2 and H_2S saturated in 1% NaCl • Exposure time = 2.5 and 28 days • Temperature = 50°C • Pressure = 15 MPa • Condition = Static	• Lesser quantity of the pozzolan cement performed better than with higher content of pozzolan material • Class G cement + Silica Fumes performed better than Class H Cement + Fly Ash
Zhang & Talman (2014)	• Three samples used: (1) Neat Class G cement (2) Class G cement + Fly Ash + 2 %Bentonite (3) Class C cement + Fly Ash + 2% Bentonite + 1% Sodium Metasiliate (lightweight cement)	• Poz mix ratio, cement to ash: (2) 59:41 (3) 59:41 •Water to solid ratio: (1) 0.44 (2) 0.554 (3) 1.130	• Cured in 0.5M NaCl • Temperature = 53°C • Pressure = 10 MPa • 25 Days	• CO_2 saturated brine • Exposure Time = 3, 7, 14, 28 and 84 days • Temperature = 53°C • Pressure = 10 MPa • Condition = Static	• Pozzolan mix sample was fully carbonated after 28 days but the durability of the pozzolan mix cement was not compromised • Lightweight cement totally lost its durability and was fully carbonated within 7 days
Aiex et al. (2015)	• Two samples prepared: (1) Neat cement (Class G cement + Pozzolan) (2) Cement Blend	• Neat Cement (Class G cement 100% + 10% Pozzolan BWOC) • Reduced Portland (Cement Blend 100%)	N/A	• Wet $scCO_2$ • CO_2 saturated DI water • Exposure Time = 12 months • Temperature = 74°C • Pressure = 14 MPa • Condition = Static	• Fresh water should be used for the cement mix rather than salt water • Reduced cement performed well w.r.t compressive strength • It shows that certain quantity of the Portland cement should be replaced with blast furnace slag or pozzolan

Authors	Preparation of the sample	Ratios of Pozzolan/water	Curing Condition	Experimental setup	Finding
Costa et al (2017)	• Two samples were prepared from class G cement with different additives that gave stable and unstable sedimentation to the cement matrix	• Water to cement ratio: (1) 0.44	• Cured in fresh water • Pressure = 14.7 PSI • Temperature = 70°C • 24 hours	•$scCO_2$ saturated in fresh water • Exposure Time = 30 days • Temperature = 70°C • Pressure = 14.7PSI • Condition = Static	• The sample with stable sedimentation showed a homogenous carbonation profile as compared to the sample with unstable sedimentation
Costa et al (2018)	• Three samples of class G cement was prepared with differ curing time	•Water to cement ratio: (1) 0.44	• Cured in fresh water • Temperature = 70°C • Pressure = 13.78 MPa • Curing time = 8hours, 7 days and 28 days	•$scCO_2$ saturated in fresh water • Exposure Time = 30 days • Temperature = 70°C • Pressure = 14.7PSI • Condition = Static	• Change in density and mass after carbonation was almost same of all the sample • Sample cured for 7 days showed slightly more carbonation then other two samples because less amount of hydrated products were formed

For non-Portland cement, the study carried by Salehi et al. (2018) compared the performance of a geopolymer cement formulated by the class F fly ash with Class H cement. It is known that the Portland cement has a brittle nature when it comes to the high temperature environment and may lose its durability Portland cement is also susceptible to corrosion which may pose by CO_2 and H_2S in the subsurface layers. The results obtained from their study indicated that the compressive strength of the geopolymer cement increases with the increase of the curing temperature. The thickening time of the geopolymer was also affected by the temperature and, as such it might be essential to use retarders to achieve a high performance geopolymer cement. It was also revealed that the geopolymer cement may shrink less than Class H cement by 2.5% when exposed to 200°F for 14 days. The transfer properties (porosity and permeability) were reduced in the geopolymer cement matrix while the reduction of the compressive strength due to the exposure to Oil Based Mud (OBM) was only 25%. A similar study was carried out by Khalifeh et al. (2018) on the rock modified geopolymer cement. The rheological measurements of the slurry showed that it has a Non-Newtonian behaviour and has a good resistance against the mechanical vibration. The cement was, however, sensitive to temperature and its thickening time could increase for 4 hours once the temperature decreased by only 10°C.

2.5 Nano Particles

In the past decade, nanoparticles have found their applications in the cement industry due to their specific and reliable functionality (Khanzadi et al., 2010). It is known that when the size of a particle is reduced to the nano scale, its chemical and mechanical properties may change due to the increase in the surface area. In addition, Calcium Silicate Hydrate (C-S-H) has been observed in a highly order structure at the nano scale which is one of the components required to resist against the carbonation taking place when the cement is exposed to $scCO_2$ (Sobolev, 2015; Singh et al., 2015).

The study carried by Jafariesfad et al. (2017) showed that addition of Nano Rubber (NR) in the cement increases the flexibility and improve the tensile strength of the cement. the experimental work was conducted under two different conditions. At first, samples were exposed only to 40°C but then the pressure and temperature was increased to 20.7 MPa and 142°C respectively. It was found that addition of NR reduces the autogenous shrinkage and the setting time. It was also observed that under the curing condition of 28 days and 40°C, the ratio of tensile stress to Young's modulus increases with the increase of NR quantity. However, carrying out curing for 3 days at the temperature and pressure of 142°C and 20.7MPa indicated that NR may not have a significant impact on the tensile strength. Although the increase in the flexibility by adding NR allows the cement to perform better when it is exposed to the tension force in the subsurface layers. There have been many nano particles proposed and used to enhance different characteristics of the cement as reported in Table 2-2.

Table 2-2: Effects of different nano particles on the cement properties (Nano Work, 2012)

Nano Materials	Effects
Nano Silica	Reducing the CO_2 propagation front by decreasing porosity and permeability; enhancing the resistance against the crack propagation; enhancing the strength and durability
Carbon nanotube	Improvement in the compressive, tensile, flexural and bending strengths; increasing the sensing ability; blast resistance; enhancing durability
Nano calcium carbonate	Improving hardness and compressive strength; decreasing the hydration period of C_3S
Polymer/clay nanocomposites	Increasing the tensile strength and heat resistance; reducing oxygen permeability,
Nano titanium	Self-cleaning; increasing the resistance to flame, corrosion and abrasion
Nano alumina	Ability to sustain drastic changes in temperature; improvement in the compressive strength, elastic modulus and thermal shocks
Nano zinc oxide	Enhancing the compressive strength and resistance against aging
Nano cellulose	Decreasing moisture absorption; increasing the bonding strength and elastic modulus

2.5.1 Proposed Nanoparticle

Nano Silica (NS) is perhaps the best option among those offered by the nano particle family because of its pozzolanic reactions and ability to improve morphological and mineralogical characteristics of the cement (Singh et al., 2013; Singh et al., 2016). There are many benefits reported to the application of NS once added to the cement (Gaitero et al., 2008; Ershadi et al., 2011; Riahi and Nazari, 2011; Sobolev, 2015; Flores-Vivián and Sobolev, 2015; Singh et al., 2015), which include but not limited to:

i) Acting as a filler and decreasing the porosity and permeability of the cement

ii) Acting as a nucleation site and compacting the cement

iii) Increasing the hydration rate of the cement
iv) Improving resistance against degradation of C-S-H
v) Pozzolanic activity and formation of secondary C-S-H
vi) Increasing the resistance against the calcium leaching
vii) Early development of strength
viii) Creation of a uniform microstructure

Gaitero et al. (2008) indicated that addition of NS significantly reduces the leaching of calcium, when it is compared to micro silica. Nano Silica also promotes a high silicate polymerization which results in formation of a long chain of C-S-H. Therefore, it seems that addition of NS improves the durability (i.e., reduction in permeability and porosity) and mechanical properties of cement (Shah et al., 2015; Flores-Vivián and Sobolev, 2015; Ershadi et al., 2011) as reported in Table 2-3.

However, due to the pozzolanic reactions posed by adding of NS, densification of the cement reduces water absorptions. Therefore, to have a better result, a proper dispersion technique must be taken for mixing NS with the cement, as otherwise agglomeration of nano particles reduces the performance of the cement as a zonal isolator.

Sonebi et al. (2015) reported that adding NS to the cement changes the rheology of the cement composite. Their study evaluated the effect of NS and superplasticizer on the plastic viscosity, flow time, yield stress and the plate cohesion meter. They highlighted that agglomeration of NS occurs because of the high surface area and existing of strong van der Waals forces between nano particles. They found that by increasing the quantity of NS, the flow time, yield stress and plastic viscosity increases while the minislump decreases (See Figure 2-3).

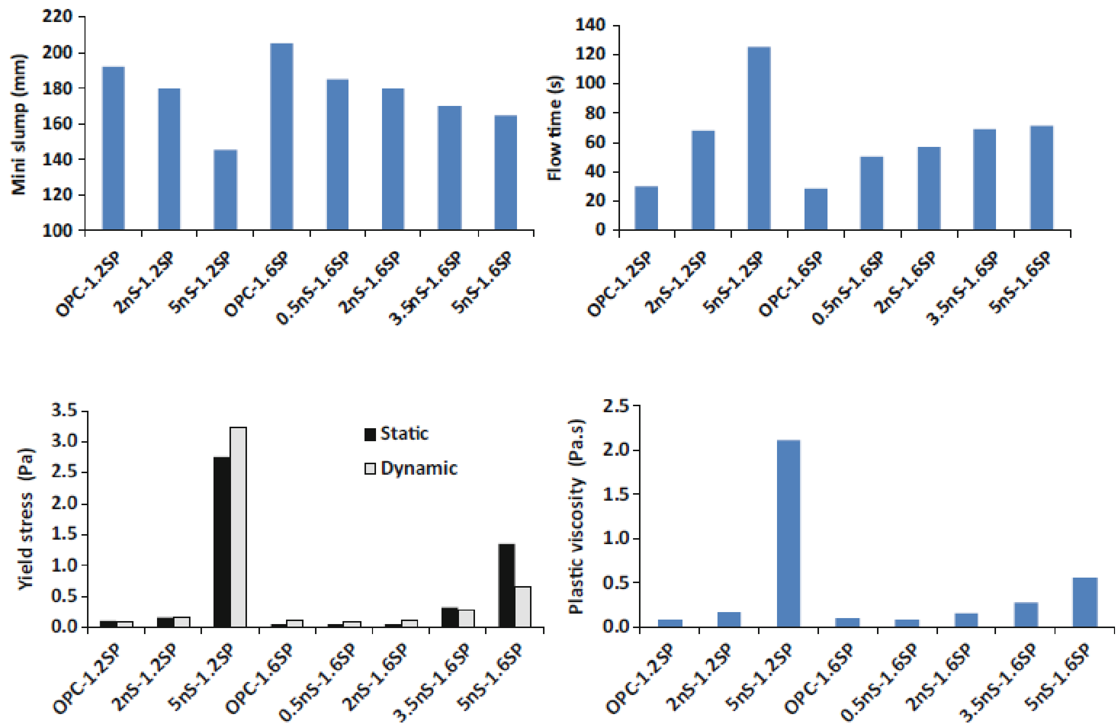


Figure 2-3: Change in rheological properties of cement by adding NS (Sonebi et al., 2015)

He and Shi (2008) compared the performance of the cement by adding different nano particles, such as TiO_2, SiO_2, Al_2O_3 and Fe_2O_3 as well as nanomontmorillonite (nano clay) to the cement. They concluded that the best performance in terms of Cl^- ion penetration and the electrical charge resistance is provided by Nano Clay and Nano Silica.

Table 2-3: Changes in the permeability and porosity of the cement by adding NS (Ershadi et al., 2011)

Slurry No.	**Porosity and permeability by adding different quantities of NS**		
	NS (%)	Porosity (%)	Permeability (mD)
S1	0	45	0.1
S2	1	30	0.001
S3	1.5	30	0.01
S4	2	29	0.019
S5	3	28.5	0.02

Lim and Modal (2015) investigated the effect of nano and micro silica in the cement samples subjected to an accelerated carbonation test. It was reported that micro and Nano Silica cement composites are better than the neat Portland cement when it comes to the carbonation depth. It was also observed that the undisturbed region (without carbonation) of samples with Nano Silica is 0.5mm away from the exposed surface while that of the micro silica and the neat Portland cement is 2 and 4mm respectively. They concluded that adding Nano Silica increases the resistance of the cement against the carbonation.

To observe the resistance of the cement against the attack of CO_2, Griffin et al. (2013) carried out experiments on the cement samples prepared by adding 1, 2 and 3 wt% NS to the class G cement cured for 28 days at the temperature and pressure of 88°C and 10 MPa respectively. After curing, samples were subjected to the carbonation test for 28 days at the temperature of 50°C and the pressure of 5-10 MPa under the dynamic condition. The result obtained showed that there is no sign of dark grey degradation propagation fronts in the sample with NS. It was concluded that the rate of degradation in the neat sample is faster than the sample bearing NS. Moreover, it was pointed that the cement sample with 1 wt% NS can provide the best performance against the attack of CO_2.

2.6 Agricultural Waste

2.6.1 Palm Oil Fuel Ash (POFA)

POFA is the by-product of the palm oil industry and is produced from the burning of palm oil plant residue. The scientific name of the palm oil tree is Elaeis Guineensis that was introduced in Malaysia in 1970. As of now, it is one of the leading cash crops in Malaysia and other tropical countries like Thailand and Indonesia. For the production of 1 ton of Palm oil, almost 5.5 tons of fresh fruit bunches are used (Oyejobi et al., 2015). Production of palm oil in Malaysia is enormous with almost 90 million tons of shells, husks, trunks, fruit bunches and palm fibers produced annually (Safiuddin et al., 2011). Husks and shells from the wastes are treated as a boiler fuel in the palm oil mills and are burned at the temperature of 800 to 1000°C to create steam that is supplied to turbines for generating electrical energy (Abdullah et al., 2006; Tangchirapat et al., 2003). The residue left after the burning is classified as Palm Oil Fuel Ash (POFA). As there is no use of POFA to the industry, it is dumped in the landfills near the palm oil mill and creates a serious environmental nuisance for the tropical countries where the production of Palm oil increases day by day. However, efforts were made in Malaysia to use POFA as the fertilizer for the agricultural industry but due to the absence of sufficient number of nutrition, POFA was not able to make its way in the agricultural industry. As of non-beneficial return, POFA is dumped near the palm oil mills, creating stern environment and health hazard (Sumadi and Hussin, 1995; Tonnayopas et al., 2006). To look into the application of POFA, attempts were made to use POFA as a supplementary cementing material (SCM) and reduce the production cost of the concrete. Moreover, POFA could reduce the amount of cement used in the concrete and make the cement production cheaper. It should also be noted that close to 5% of total CO_2 emission to the atmosphere is coming from the production units of the cement which can be reduced if POFA can replace the cement (Subhashini and Krishnamoorthi, 2016).

Considering the fact that POFA is dominated by silica in its composition, as mentioned earlier there have been many attempts to show the application of POFA as a supplementary cementing material (SCM) in the cement and concrete industry. For instance, Tay (1990) used ungrounded POFA to replace the cement and concluded that due to the low pozzolanic activity, only 10% 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 the 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 the control sample. They observed that the cement based POFA with 15 wt% replacement was the best samples in terms of the compressive strength and workability. Bamaga et al. (2013) carried out a series of experiment on the concreter made by POFA and compared its performance with the control sample. They indicated that the strength development 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 behaved 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, a reduction in the heat 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 discovered that a high percentage of POFA replacement gives a high workability to the concreter due to the superplasticizer effect. It was also 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 a deleterious effect on the concrete strengths. Oyejobi et al.

(2015) observed that the strength of the POFA based cement composite is lower than the control sample and the strength of the samples dropped as the quantity of POFA increases. Subhashini and Krishnamoorthi (2016) observed that the best compressive, flexural, and tensile strength is achieved with a cement composite bearing 20 wt% POFA. Having said that, POFA has not been properly introduced to the petroleum industry as a supplementary cementing material (SCM) for oil well cementing. Considering its low price and significant physical property enhancement, it could be a great asset for the completion of well exposed to the acidic environment.

2.6.2 Rice Husk Ash (RHA)

Rice is one of the most important staple foods for the world population and its demand will continue to increase in the coming future as the population of the world is on the rise. According to Timmer et al. (2010), consumption of the rice in 2020 will be around 450 million tons which is 6.6% more than the consumption of the rice recorded in 2007 (422 million tons). More than 20 to 33% of the rice paddy weight is coming from husk which contribute to 137 million ton of waste production globally (Lim et al., 2012). The solid waste of the rice husk creates an environmental nuisance around the world that requires serious attention. As such, a series of research work was carried out on the potential applications of rice husk and it was discovered that it can be used to generate electrical energy and can produce ethanol (Kim and Dale, 2004). Moreover, it was found by Xu et al. (2012) that rice husk can be used as a partial replacement in the cement to improve the physical and mechanical properties of the concrete. Adding RHA to the cement helps to reduce the amount of CO_2 emission produced by the cement factories and can, in the meantime, reduce the cost of the cement (Mehta, 2002; Sudendro, 2014).

Since Rice Husk Ash (RHA) is characterized as a pozzolanic material it can be one of the good options to improve the cement resistance. As a matter of fact, once burned, lignin and cellulose present in RHA which can be as much as 50% that can be converted to silica and provide pozzolanic reactions. However, the method by which the RHA is burned dictates the structure (crystalline or amorphous) and the reactivity of RHA. The burning of RHA can take place in a controlled or uncontrolled way. In the uncontrolled method, the burning of the rice husk takes place in the open field while in the controlled method, the burning of the rice husk is induced for certain period of time under certain temperature. It is shown by Christopher et al. (2017) that the uncontrolled burning of the rice husk in the open field will produce crystalline structure which once added/replaced in the cement/concrete will impede the development of the strength in concrete/cement. From the above discussion, it is clear that the pozzolanic activity will be effective if the structure of the rice husk will be under the amorphous state. Other than that, the research carried by Le (2015) and Antiohos et al. (2014) showed that the pozzolanic activity of RHA is also dependent on the particle size. Thus, to achieve the amorphous structure of RHA, the controlled burning (specific time and temperature) method should be considered. The research carried by different authors have shown that the incineration should not exceed 700°C in order to have amorphous silica in the RHA (Ahmed and Adam, 2007; Nair et al., 2008). However, if the burning temperature should go above 700°C, the time duration of the incineration should be kept short (Maeda et al., 2001).

Zhang and Malhotra (1996) did the test on several cement samples prepared by adding 10 wt% RHA and silica fume. It was found that after 28 and 180 days of curing, the compressive strength of the RHA based concrete is higher than the control sample but less than the sample with silica fume. It was also revealed that after 28 and 90 days of curing, RHA based samples perform better compared to the control sample in the ion penetration tests. Salas et al. (2013) reported the laboratory test done on the concrete with 5 to 20 wt% of RHA and 10 wt% silica fumes. RHA used in their studies was thermally and chemically treated. The study focused on the mechanical and transport properties of the concrete and it was observed that concrete containing 10 wt% chemically treated RHA has a higher compressive strength, flexural strength and elastic modulus than the control cement and silica fume concrete composite. As for the transport properties, it was found that the RHA based concrete composite can perform better with in the chloride penetration, carbonation and water absorption tests. Studies carried out by Ahmad et al. (2014) showed that 5 wt% RHA in concrete gives a good resistance against the acidic environment when they exposed their samples to an acidic fluid with the pH of 3 to 4 for 90 days. Soares et al. (2015) performed an experimental investigation on well cement having RHA composition. They stated that adding RHA in the well cement increases the compressive strength and reduces the quantity of Portlandite, resulting in a better performance. This was, however, the only study reported so far evaluating the impact of RHA on a well cement (Class G) cured under the HPHT condition. Zareeia et al. (2017) replaced cement with RHA from 5 to 25 wt% and did a series of tests that include mechanical tests (compressive and tensile strength), water absorption and permeability test. It was found that the mechanical strength for all the replacement level of RHA was higher than that of the control sample where 15 and 20 wt% RHA showed the highest mechanical properties. However, mechanical properties started to deteriorate as the replacement level went above 20%. On the other hand, for the water absorption and permeability tests, it was fond that as the quantity of RHA increases, the water absorption and permeability reduce by as much as 26% and 78% respectively compared to the control sample. Christopher et al. (2017) pointed out that at least 10 wt% of RHA is required to have a good development of the compressive strength. Kannnan (2018) carried out experiments on the mechanical, durability and fresh properties of the cement where self-combusted rice husk ash was used as the replacement in the cement in the range of 0 to 30 wt%. He observed that the best result is obtained if the cement has 15% RHA. Later, Thomas (2018) concluded that the workability of the concrete is not hampered when RHA is used at the replacement level of 5 to 10 wt%. It appeared that above that level, the workability of the concrete starts to increase and superplasticizer must be used. Having said that, more studies are required to show the application of RHA in oil well cementing when cement are exposed to HPHT and acidic environment of storage sites.

2.7 Conclusion

Given the literature review provided, it is observed that cement exposed to dry/wet $scCO_2$ in a storage site condition may go through a severe degradation. Technically speaking, it seems that carbonation of the cement at the early stage of degradation is a self-healing process and improve the physical (permeability and porosity) and mechanical (compressive and tensile strength) properties of the cement. However, as the ingression of $scCO_2$ continues, $CaCO_3$ will be transformed into calcium bicarbonate and will be leached out of the cement matrix resulting in significant reduction of cement durability. Once Portlandite is consumed, dry/wet CO_2 attacks C-S-H, which is the main binding material in the cement structure and converts it into amorphous silica gel which further compromises the strength of the cement matrix.

Different authors proposed different approaches to improve the cement resistance against CO_2 attack, where adding pozzolanic materials was found to be the best method. It should be noted that Portlandite is the most vulnerable component during the attack of CO_2 and its reduction by inducing pozzolanic reactions can help the cement to have a higher resistance. Nonetheless, complete removal of Portlandite from the cement matrix accelerates the carbonation and degradation process. As such, certain quantity of Portlandite should be left in the cement to slow down the carbonation process. This topic will be further discussed in the next chapters where attempts are made to show how pozzolanic materials such as Nano Silica, POFA and RHA can be used to improve the physical characteristics of the cement against the acidic environment.

Chapter 3: Application of Nano Silica in Oil Well Cementing

3.1 Introduction

Although there have been several studies on the application of Nano Silica (NS) in oil well cementing, the quantity of this nano material which should be added to the cement under different circumstances has not been well understood. This might be linked to the difficulty of NS dispersion or identification of its quantity to have the best performance during and after consolidation (Santra et al., 2012). For instance, it has been indicated that this quantity should be close to 1% By Weight of Cement (BWOC) in few studies (He and Shi, 2008; Ershadi et al., 2011; Santra et al., 2012), while Rahman et al. (2015), who designed a cement for a High Pressure (8000-9000 psi) High Temperature (290°F) well in Saudi Arabia highlighted that the quantity of NS must be at least 2 wt% to achieve the best performances. In addition, most of these studies are using an old fashion approach to mix NS with the cement which, as it will be shown later, is not capable of providing consistent results.

In this study, several tests were conducted on the NS based cement prepared by two different mixing techniques. The first technique follows the literature mixing while the second was developed in this study and is referred to as a new mixing technique to achieve a better result. Furthermore, the effect of changing the parameter of sonication method is highlighted to have a broader and better understating on the effect of NS dispersion in the cement. The tests conducted to evaluate the cement samples mainly consist of rheology, density, compressive strength, WOC, XRD, TGA and SEM tests.

3.2 Materials and Methods

Class G cement was used for the purpose of this study with a Blaine specific surface area of 280-340 m^2/kg (Kurdowski, 2014). The specific surface area of the Nano Silica was around 170-200 m^2/g and its size varied from 15nm to 20nm with the purity of 99.5%. Table 3-1and Table 3-2 summarise the chemical and physical composition of the cement used.

Table 3-1: Chemical compositions of Class G cement used in this study (Smith, 1990)

Compound	Content (wt %)
Silicon Dioxide (SiO_2)	21.7
Calcium Oxide (CaO)	62.9
Aluminium Oxide (Al_2O_3)	3.2
Iron Oxide (Fe_2O_3)	3.7
Magnesium Oxide (MgO)	4.3
Sulfur Trioxide (SO_3)	2.2
Total alkali as Na_2O	0.54
Loss on ignition	0.74
Insoluble residue	0.14

Table 3-2: Class G cement compositions (Adams, 1985, Smith, 1990)

Compound	Cement Chemist Notation	Content (wt %)
Tricalcium Silicate $(CaO)_3 . SiO_2$	C_3S	58
Dicalcium Silicate $(CaO)_2 . SiO_2$	C_2S	19
Tricalcium Aluminate $(CaO)_3 . Al_2O_3$	C_3A	2
Tetracalcium Aluminoferrite $(CaO)_4 . Al_2O_3 . Fe_2O_3$	C_3AF	11

3.3 Preparation of Cement Samples

3.3.1 Literature Mixing Technique

To prepare the cement samples required to conduct the tests, neat cement (i.e., cement without any additives) were mixed with water according to the API Standard 10-A (2005) with a water to cement (w/c) ratio of 0.44. This ratio was maintained when cement was replaced with different quantities of NS as reported in Table 3-3.

Table 3-3: Cement composites used for the purpose of this study

Sample No.	Content of Nano Silica (wt%)	Weight of Nano Silica (g)	Weight of cement (g)
1	0	0	692
2	0.25	1.73	690.27
3	0.5	3.46	688.54
4	0.75	5.19	686.81
5	1	6.92	686.81
6	1.5	10.38	681.62

As per the literature, the agglomeration of Nano Silica would not have any deleterious effects on the cement properties (Choolaei et al., 2012). Hence, Nano Silica can be manually mixed with the cement and added to water. Preparation of the slurry is done in the last stage by a 3 minutes mixing at the speed of 4000 rpm which is followed by a high-speed mixing at 12,000 rpm for 35 seconds (Ershadi et al., 2011; Rahman et al., 2015). This approach, in this study, is referred to as the literature mixing technique. Figure 3-1 shows the steps taken in the literature mixing technique.

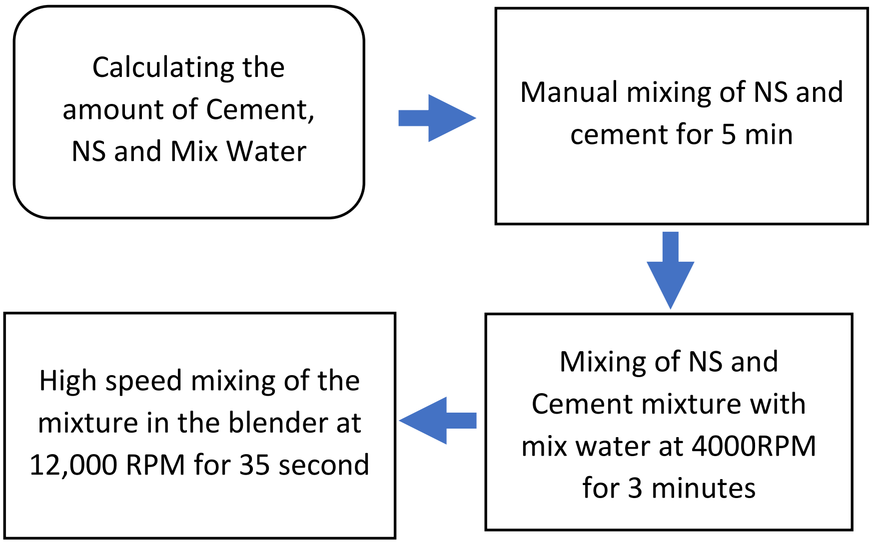


Figure 3-1: Steps involved in the literature mixing technique

3.3.2 A New Mixing Approach

In this approach, which was developed executively for the purpose of this study, the given amount of Nano Silica added to water was stirred with a homogenizer at the speed of 5000 rpm for 15 min. This was to break the lumps of Nano Silica formed when it is added to water.

It should be noted that Nano Silica has a hydrophilic nature and can agglomerate or flocculate when it is exposed to water. After homogenization, the solution was subjected to ultrasonic dispersion. The dispersion was done for 30 minutes with the help of a Sartorius Labsoni®M sonication probe under the amplitude of 100%. The cement was then added to the dispersed solution and mixed with a constant speed mixer at the speed of 4000 rpm for 3 minutes and 12,000 rpm for 35 seconds using the Fann constant speed mixer (Model 686CS) shown in Figure 3-2. This approach is referred to as the new mixing technique in this study. Figure 3-3 presents the steps involved in the new mixing technique.

Figure 3-2: Fann constant speed mixer used for the purpose of this study

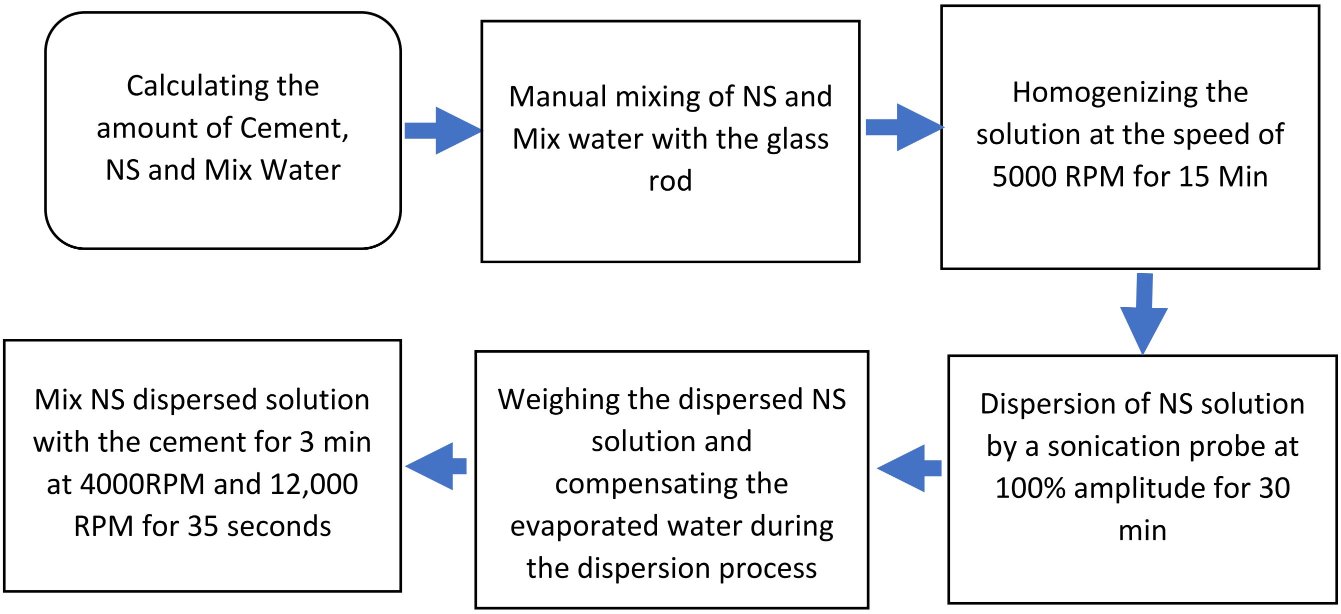


Figure 3-3: Steps involved in the new mixing technique

3.4 Experimental Results

3.4.1 Rheological Properties

Characterization of rheological parameters is an integrated part of the cement design where determination of the frictional pressure loss and pumping horsepower is highly demanded. There are, generally, two mathematical models commonly used to highlight the rheological parameters of a cement slurry known as Bingham plastic and Power law (Nelson, 1990). In the Bingham plastic, a plastic viscosity and yield point are determined as the slope and intercept of the graph created after plotting the shear rate against the shear stress. On the other hand, the power law model is represented by two parameters, k and n. The parameter k is also known as the consistency index and is proportionally related to the apparent viscosity. The degree of the non-Newtonian behaviour in the fluid is often expressed by the parameter n, which is a dimensionless quantity (Nelson, 1990).

The rheological measurements were made using the rotation viscometer of Fann Model 35 shown in Figure 3-4. Prior to rheological measurements, the conditioning of the cement slurry was done according to the API Standard 10-B (2013) in a Fan Atmospheric Consistometer. The slurry was then poured in the viscometer cup and the reading were recorded at different speeds except 600 rpm. It should be noted that it is not advised to have any readings at 600 rpm as it may degrade the cement properties and give erroneous results (API Standard 10-B, 2013). Both of the mixing approaches, literature and new mixing, described earlier were used for the preparation of the samples and the measurements of the rheological parameters. Figure 3-5 compares the rheological parameters obtained for the samples having 0.25 wt% and 0.5 wt% Nano Silica prepared by the literature mixing technique. Table 3-4 summarises the results obtained for different cement composites prepared by the literature mixing technique.

Figure 3-4: Fann viscometer (left) and Fann atmospheric consistometer (right)

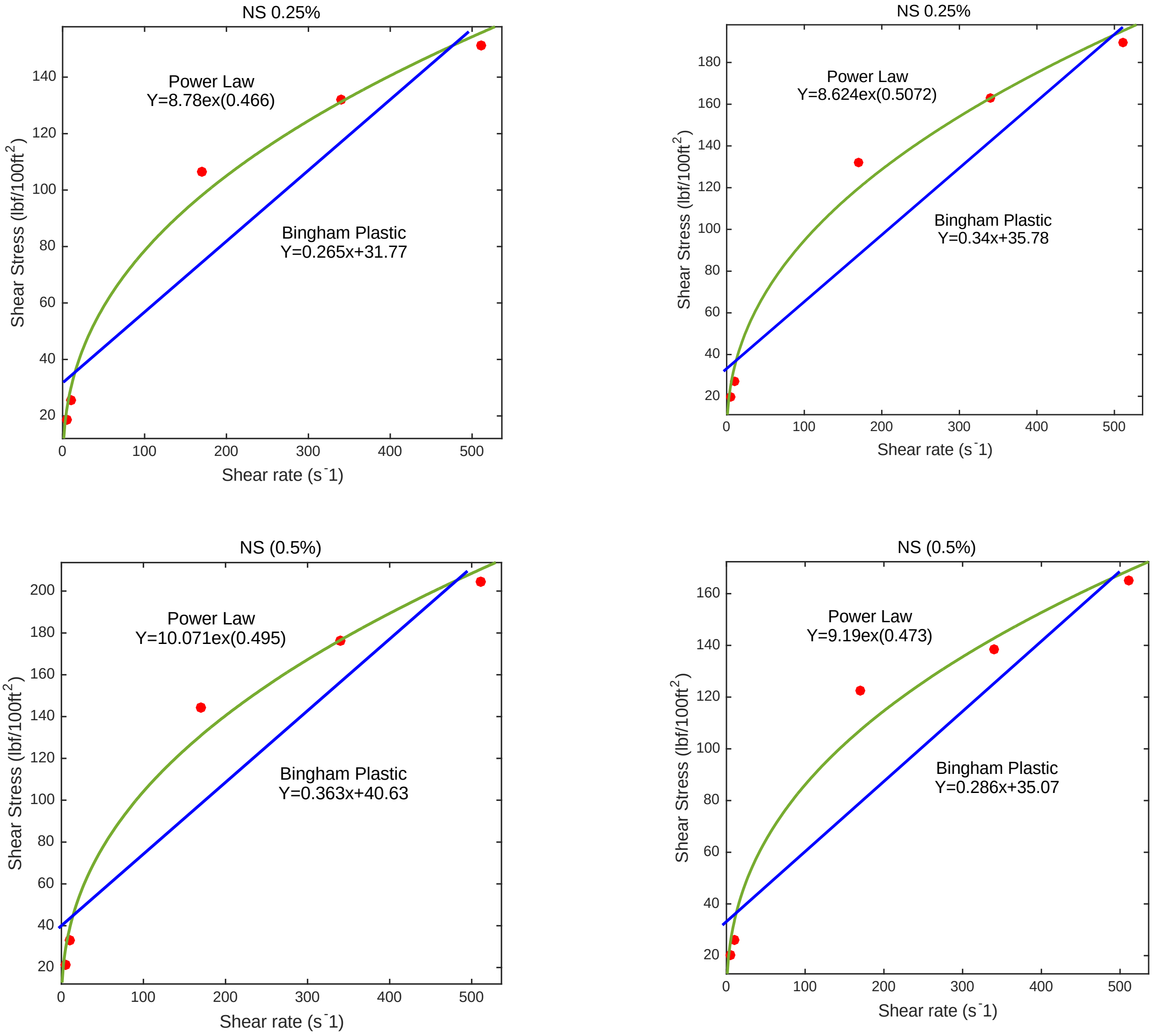
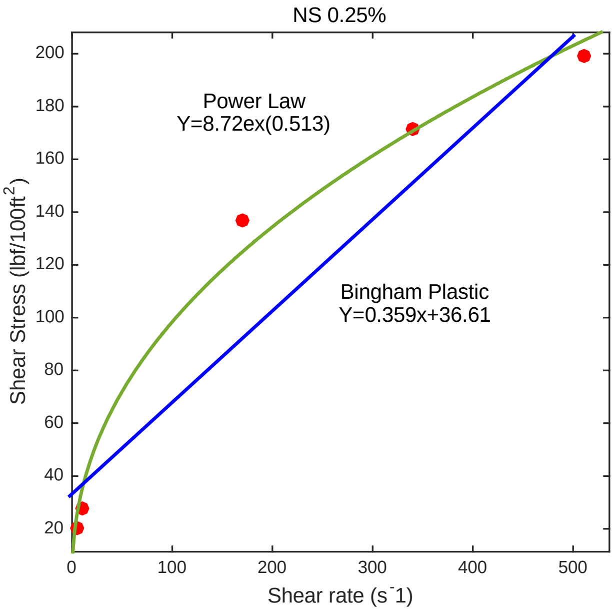


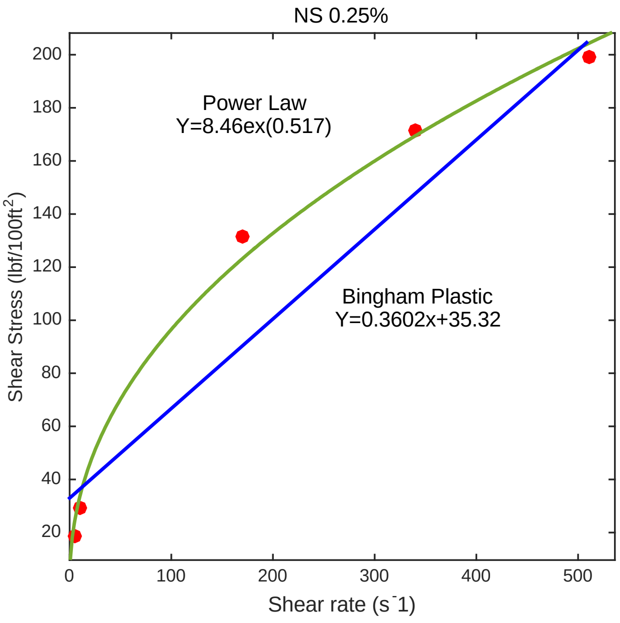
Figure 3-5: Rheological parameters and the models obtained from adding 0.25 wt% and 0.5 wt% Nano Silica into the cement using the literature mixing

Table 3-4: Rheological parameters of the cement composites prepared by the literature mixing

Sample No. (Replacement level of NS %)	Plastic Viscosity (cP)	Yield Point (lb/100ft^2)	k (lbf-sec/100ft^2)	n
2a (0.25%)	127.07	31.78	8.78	0.466
2b (0.25%)	162.84	35.789	8.62	0.5072
3a (0.5%)	173.8	40.639	10.07	0.495
3b (0.5%)	137.22	35.073	9.19	0.4736

From Table 3-4, it is observed that the difference between the plastic viscosity and the yield point of the cement with a similar quantity of Nano Silica mixed by the literature mixing is more than 20% and 10%, respectively. This discrepancy might be catastrophic when a cement slurry is prepared in the rig site based on the recipe received from the laboratory measurements. Therefore, a better technique is required to provide more consistent results when Nano Silica is used as a replacement in the cement composition. The rheological parameters obtained from the cement composites prepared by the new mixing technique are depicted in Figure 3-6 and summarised in Table 3-5.





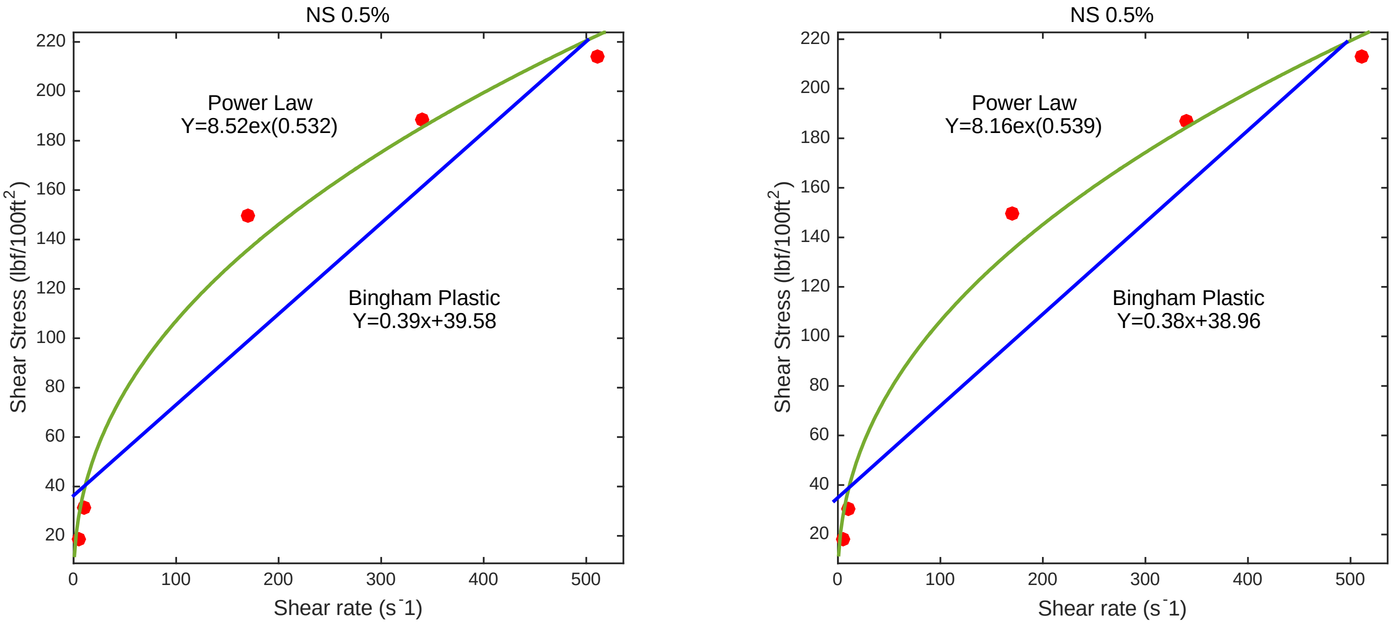


Figure 3-6: Rheological models obtained from adding 0.25 wt% and 0.5 wt% Nano Silica to the cement using the new mixing approach

Table 3-5: Rheological parameters of cement composites prepared by the new mixing approach

Sample No. **(Replacement level of NS %)**	**Plastic Viscosity (cP)**	**Yield Point (lb/100ft^2)**	**k (lbf-sec/100ft^2)**	**n**
2c (0.25% NS)	172.03	36.619	8.72	0.513
2d (0.25% NS)	172.51	35.329	8.46	0.517
3c (0.5% NS)	186.82	39.584	8.52	0.5329
3d (0.5%NS)	186.25	38.96	8.16	0.5395

Summarised in Table 3-5, the new mixing technique is able to give a very consistent result in terms of plastic viscosity and yield point for the samples with the same amount of Nano Silica. Having achieved the consistency in the rheological parameters, attempt was made to determine the minimum amount of Nano Silica required to achieve the best results with the lowest cost. To do this, up to 1.5 wt% Nano Silica replaced the cement, as reported in Table 3-3 and changes in the rheological parameters were monitored. Table 3-6 reports the results obtained from these measurements.

The results obtained indicated that as the quantity of Nano Silica increases, the plastic viscosity and yield point increases with the highest plastic viscosity and yield point observed for the cement composite with 1.5 wt% Nano Silica. In fact, the cement composite with 1.5 wt% Nano Silica was so thick and was not flowing even when the whole beaker was turned upside down as shown in Figure 3-7.

Table 3-6: Rheological properties of the cement composites prepared by the new mixing approach

Nano Silica content (wt%)	Mixing Technique	Plastic viscosity (cP)	Yield point (lb/100ft^2)	k (lbf-sec/100ft^2)	n
0	API Standard	146.22	33.82	9.8	0.5697
0.25	New Mixing	172.51	35.329	8.4	0.517
0.5	New Mixing	186.25	35.969	8.1	0.5395
0.75	New Mixing	203.49	36.842	7.4	0.5636
1	New Mixing	212.06	38.24	7.4	0.5697
1.5	New Mixing	251.08	42.329	7.5	0.5963

Figure 3-7: Thick cement composite having 1.5% of NS in its structure

Looking at Table 3-6 and the lab observations made, it was concluded that the quantity of Nano Silica should not exceed 1 wt% in the cement slurry, as otherwise its pumping may cause difficulty on site.

3.4.2 Density

Density is another crucial parameter of the cement design which indicates the pressure applied by the cement on the formations during the placement. This pressure must not be higher than the fracture pressure, as otherwise extensive fluid loss can be experienced. It was, therefore, crucial to ensure that adding Nano Silica to the cement is not causing any significant changes in the density. The cement density was measured using the Fann Mud Balance TruWate Model 141(see Figure 3-8) and the results are summarised in Table 3-7.

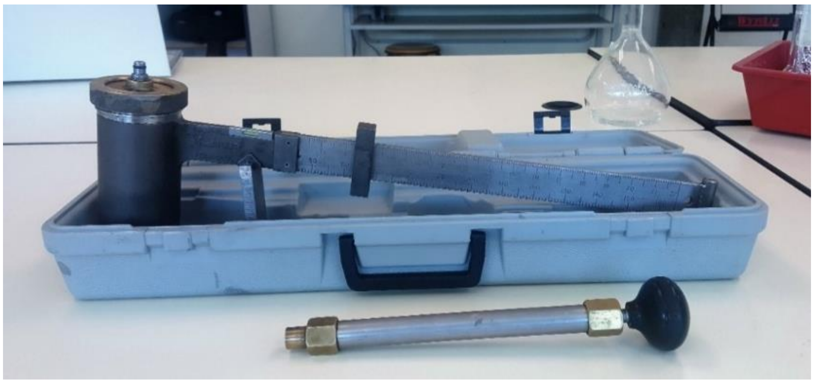


Figure 3-8: Fann Mud Balance TruWate Model 141 used for the measurement of the cement composites

Table 3-7: Density of Nano Silica-based cement composites

NS Content (wt%)	Density (PPG)	Specific Gravity
0	15.5	1.86
0.25	15.4	1.85
0.5	15.3	1.84
0.75	15.4	1.85
1	15.3	1.84

As seen in this Table 3-7, the density of the cement composites with different amount of Nano Silica is almost as same as that of the neat cement. This is mainly because the quantity of the cement replaced by Nano Silica is very small and cannot have any impacts on the density.

3.4.3 Compressive Strength

Compressive strength is another important property for the cementing design which indicates the maximum stress sustained by the cement before failure. To evaluate strength development in real time, Ultrasonic Cement Analyser (UCA) Model 3504 was used as shown in Figure 3-9. 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 before next phase of drilling start). The test was carried out for 8 hours at the reservoir condition where the temperature and pressure reached to 50°C and 2200 psi respectively for different cement composites.

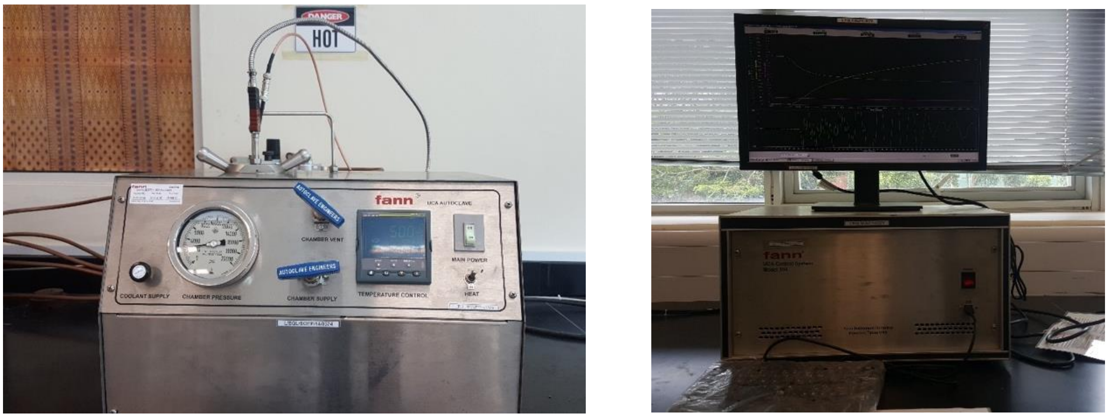
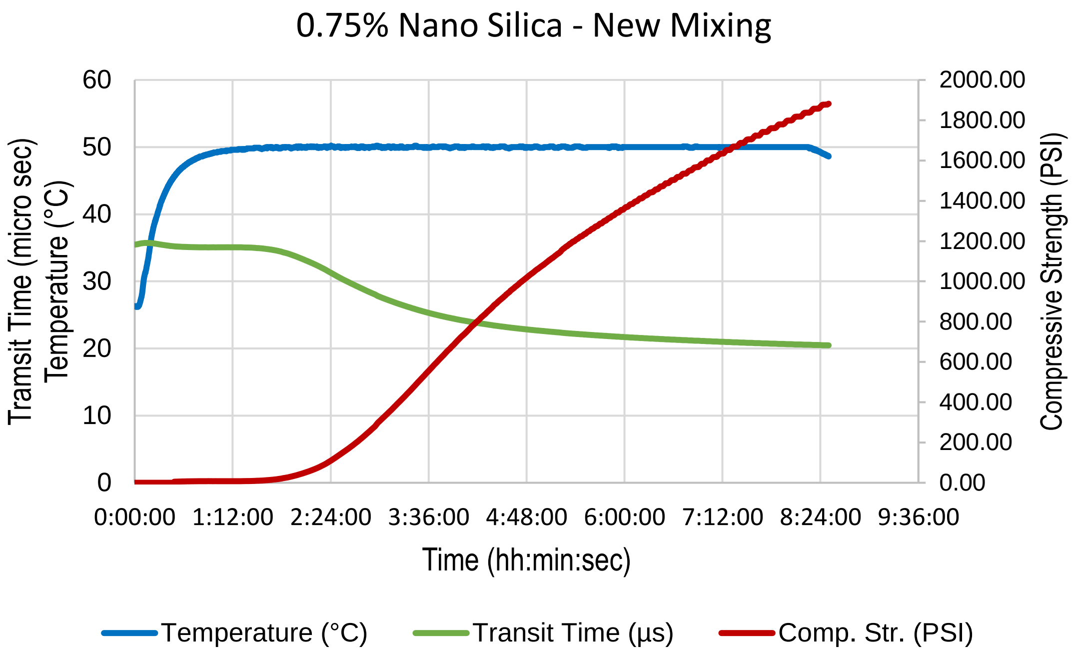


Figure 3-9: Ultrasonic Cement Analyzer (UCA) used for determination of the compressive strength

The results obtained indicated that the compressive strength of the cement prepared by the literature mixing is almost 200 psi lower than the one prepared by the new mixing technique (See Figure 3-10). It was also found that regardless of the mixing approach, the compressive strength of the cement with Nano Silica was higher than that of the neat cement.



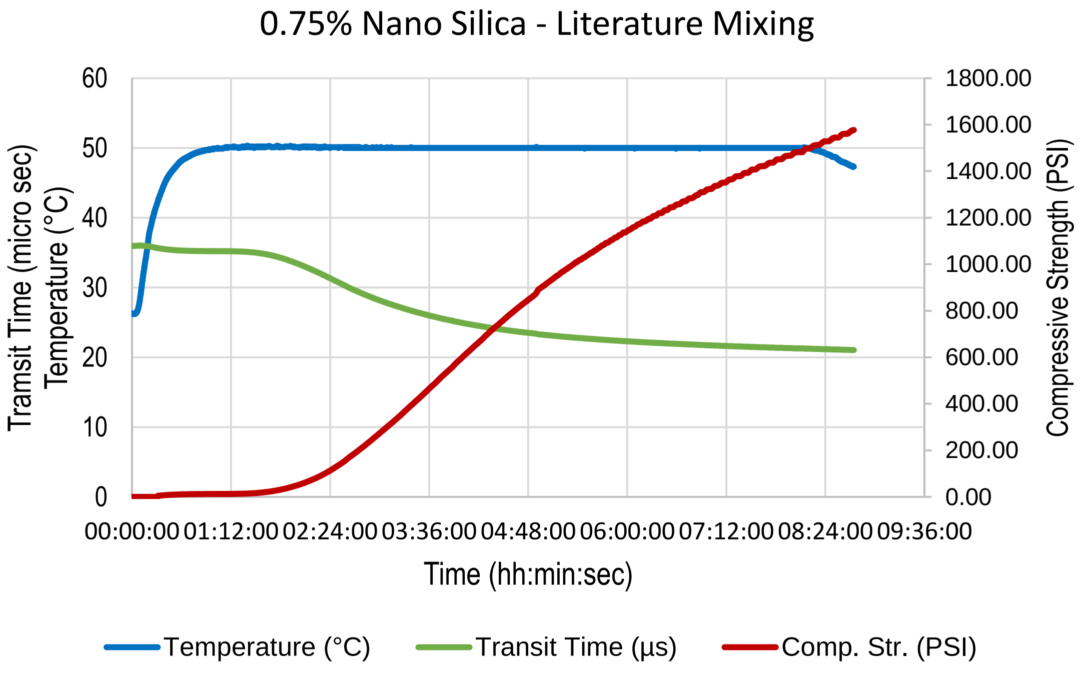


Figure 3-10: Compressive strength of the cement composites prepared by the literature and new mixing approaches

It was also noted that Nano Silica would contribute into the cement strength development up to a certain level which turned out to be 0.75 wt%. In fact, the cement composite with 1 wt% Nano Silica appeared to have a lesser strength than the cement bearing 0.75 wt% Nano Silica (See Figure 3-11). This was the same conclusion made by Singh et al. (2016) as they stated that from a certain point Nano Silica will not contribute into the strength development. It should be noted that due to the high viscosity and yield point of the cement with 1.5 wt% Nano Silica, it was not subjected to the compressive strength test in this study.

Further evaluations of the results revealed that regardless of the mixing techniques employed, the WOC of the cement composites is shorter than that of the neat cement. However, between two different mixing techniques, the cement slurries prepared by the new mixing technique, except the one having 1 wt% Nano Silica, had a shorter WOC time than the one prepared with the literature mixing. Hence, the new mixing approach was indicated to be a better method compared to the literature mixing when it comes to the compressive strength and WOC. Table 3-8 summarises the WOC of different cement composites.

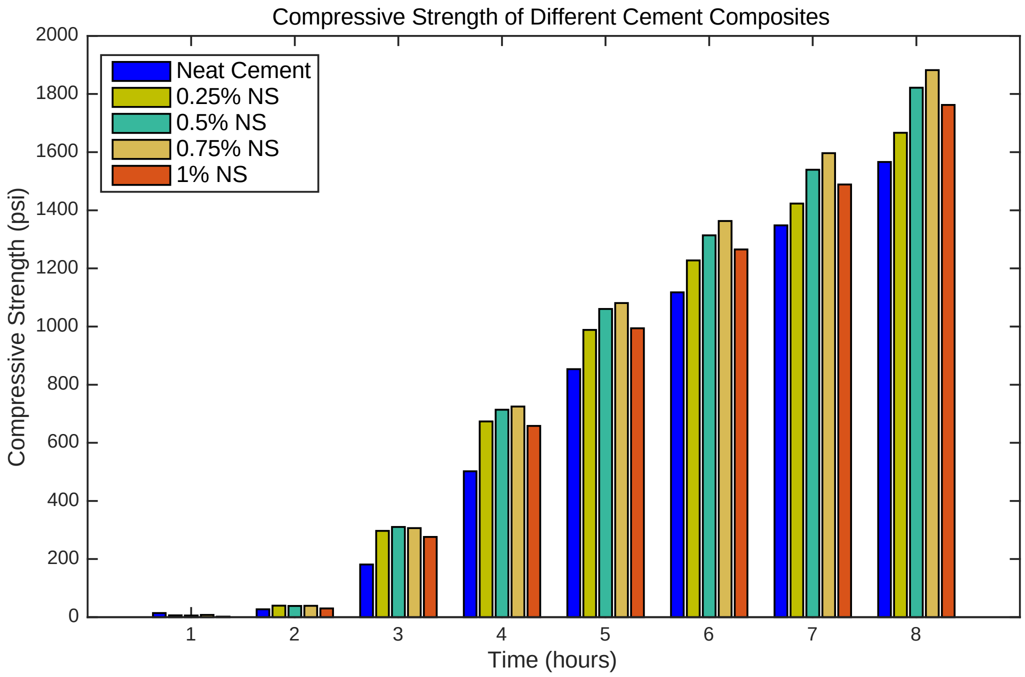


Figure 3-11: Compressive strength development of different cement composites

Table 3-8: WOC of the cement composites prepared by different mixing techniques

Nano Silica Content (%)	WOC, Literature Mixing (HH:MM: SS)	WOC, New Mixing (HH:MM: SS)
0.25	03:40:21	03:33:01
0.5	03:37:22	03:28:22
0.75	03:42:22	03:28:22
1	03:26:40	03:34:40

Comparing the compressive strength and WOC of different cement composites, it seems that the composite with 0.75 wt% Nano Silica would be the best choice to have the highest strength development in a shorter period of time.

3.4.4 Thermogravimetric Analysis (TGA)

Characterization of the cement composites was carried out by a Mettler Toledo Thermo Gravimetric Analyser (TGA) as shown in Figure 3-12. TGA is able to measure the mass loss when the cement is subjected to heat. For the purpose of this study, dehydroxylation of Portlandite was required and TGA was a perfect tool to monitor it. According to the literature, the temperature at which the dehydroxylation of Portlandite takes places varies from 400 to 500°C while the rate of increase in the temperature should be 10°C/min with the nitrogen flow of 50ml/min (Garnier et al., 2010; Lim and Mondal, 2015).

Figure 3-12: Mettler Toledo Thermo Gravimetric Analysis (TGA) used for the material characterization

Due to the pozzolanic reaction caused by adding Nano Silica, the quantity of Portlandite decreases and the amount of this decrease must be known as it plays an important role when the cement is exposed to $scCO_2$. To measure the quantity of Portlandite (CH (%)) left in the samples, the following equation was used (Jain and Neithalath, 2009; Lim and Mondal, 2015):

$$CH\ (\%) = WL_{(CH)}\ (\%) * MW_{(CH)}/MW_{(H)} \qquad (3\text{-}1)$$

where WL $_{(CH)}$ is the percentage weight loss during the dehydroxylation of $Ca(OH)_2$, MW $_{(CH)}$ and MW $_{(H)}$ are the molar weight of $Ca(OH)_2$ and water respectively. Table 3-9 gives the results obtained from the TGA test on the samples.

The results obtained indicated that as the amount of Nano Silica increases, the quantity of Portlandite decreases. However, it should be noted that too much reduction of Portlandite may increase the rate of cement degradation when it is exposed to $scCO_2$ (Brandl et al., 2011). Although Portlandite reduction is good to have a higher stress resistance, it must not be totally removed as it slows down the carbonation process. From the discussion above, it can be concluded that adding 0.75 wt% Nano Silica to the cement is the best choice as it provides a good rheological and strength behaviour without significant reduction of Portlandite.

Table 3-9: Percentage of Portlandite in the cement composites

Nano Silica content (%)	**WL $_{(CH)}$ (%)**	**CH (%)**
0	3.06	12.58
0.25	2.86	11.75
0.5	3.04	12.49
0.75	2.82	11.59
1	2.61	10.73
1.5	2.43	9.99

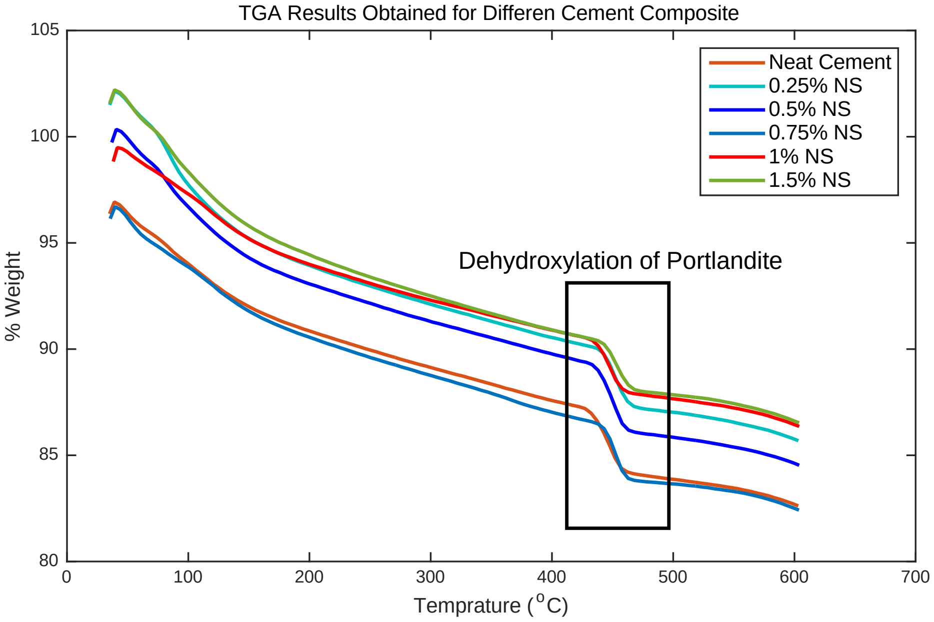


Figure 3-13: TGA curves showing the weight loss of different cement composites

3.5 Dispersion Parameters

To show the effect of dispersion on the cement composites, attempts were made to change the parameters of dispersion including the amplitude and time. The machine used for the dispersion of Nano Silica was ultrasonic machine model LSP-500 Laboratory-Scale Processor shown in Figure 3-14. The results obtained indicated that if the amplitude decreases to 60% and time of dispersion reduces by 15 min, a lower compressive strength is obtained compared to the dispersion made at the amplitude of 100% for 30 min (See Figure 3-15).

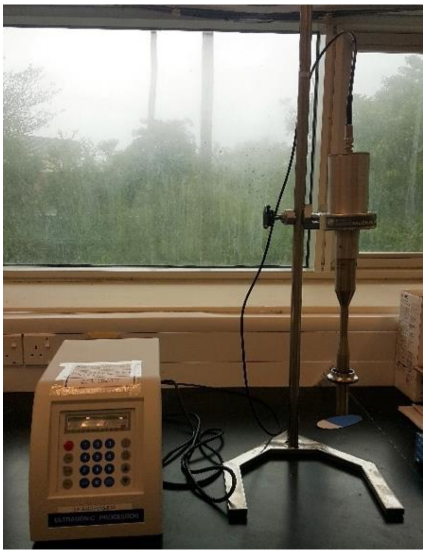


Figure 3-14: LSP-500 Laboratory-Scale Processor used for the dispersion of NS

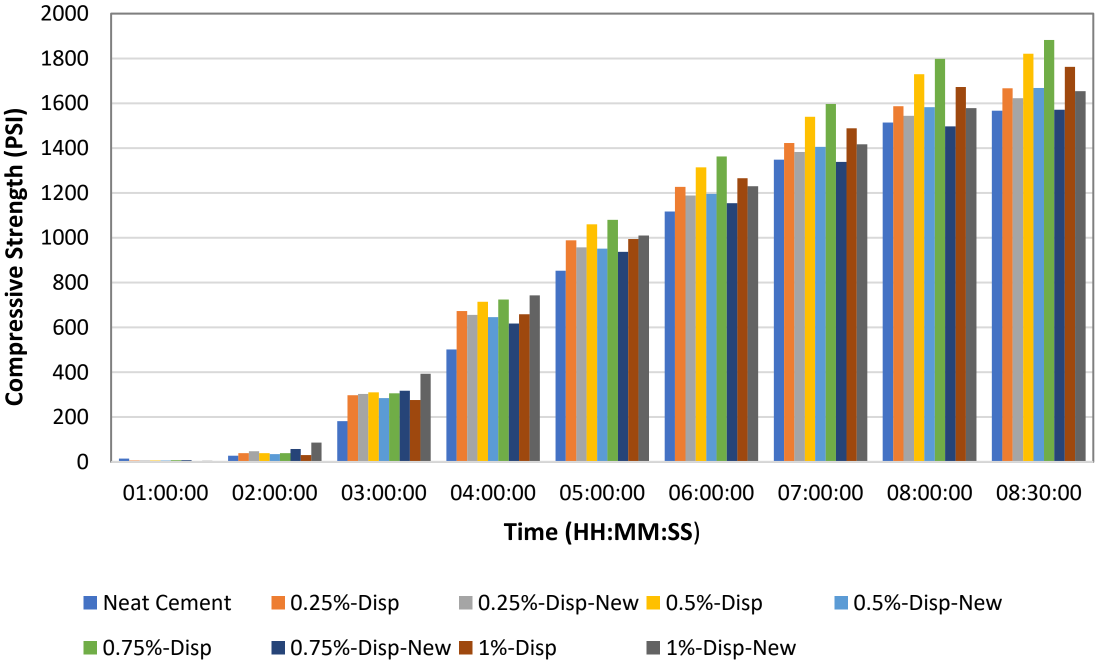


Figure 3-15: Compressive strength of different dispersion techniques for 8 hours

However, the new dispersion technique had a higher compressive strength when 0.5 wt% Nano Silica was replaced in the cement after 24 hours as shown in Figure 3-16. In the next stage, this new dispersion methodology was compared with the old dispersion technique to evaluate the compressive strength development for 8 hours (See Figure 3-15). It was then found that the best compositions from the literature and new dispersion technique are those with 0.5% Nano Silica replacement. After eight hours of testing, it was, however, revealed that the new dispersion technique gives a higher compressive strength than the literature mixing with the difference that could go to up to 6.31% after 24 hours (See Figure 3-17). This indicated that regardless of the dispersion technique being used, the compressive strength obtained by the new mixing method is always higher than the literature mixing. To support the results, TGA tests were conducted on the 0.5% Nano Silica based cement prepared by the new and literature mixing method. It was then found that a lower amount of $Ca(OH)_2$ is produced with the new dispersion technique compared to the literature mixing, although the difference seems to be only 1%. It should be noted that the solid volume percentage of $Ca(OH)_2$ in the hydrated cement varies from 20 to 25% and this even 1% decrease in the Portlandite quantity may make lots of difference.

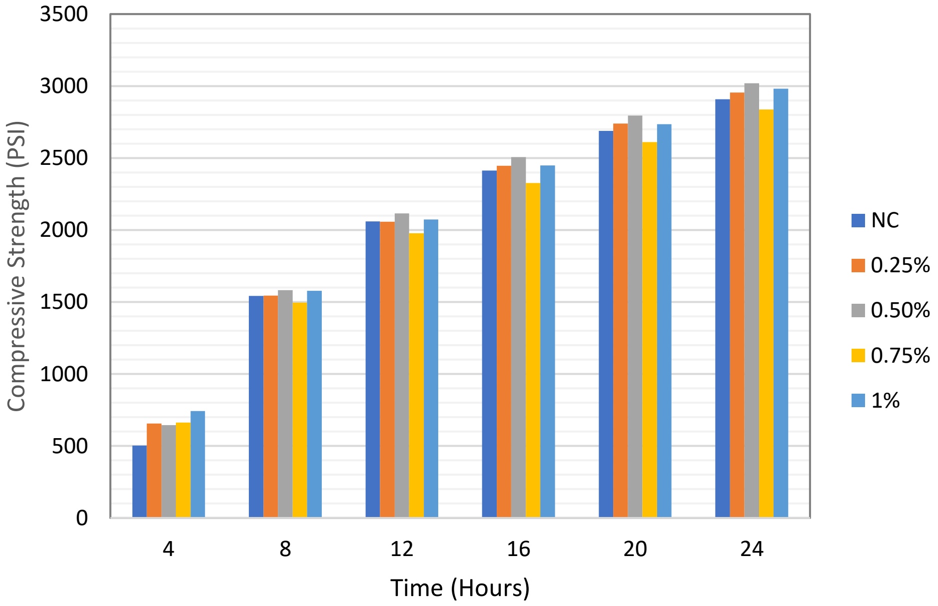


Figure 3-16: Compressive strength of the cement prepared by the dispersion technique with changed parameters after 24 hours. NC is standing for Near Cement in the legend

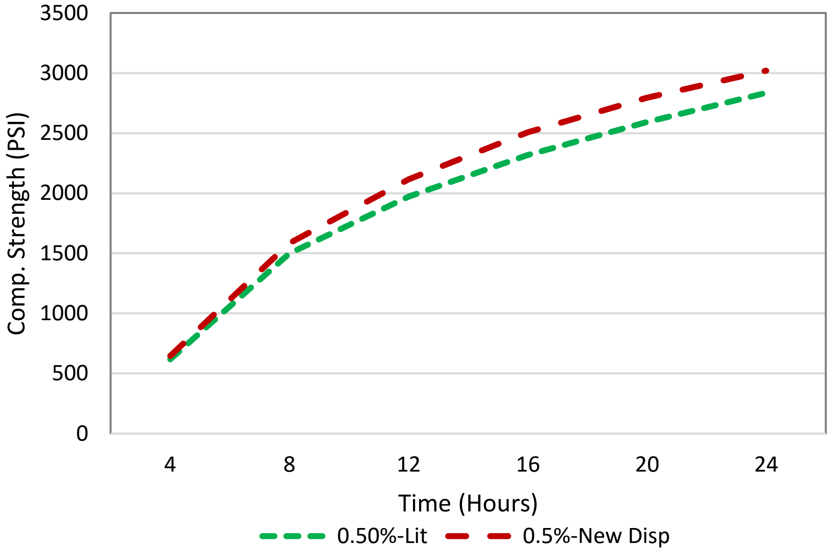


Figure 3-17: Comparison of the strength development in the samples with 0.5 wt% NS prepared using two different mixing techniques

3.6 XRD Analysis

To have further conformation on the amount of Portlandite left in the samples, XRD analysis and RIR based interpretation were conducted. It was observed that even after 3 months of curing, the amount of Portlandite left in the samples was less in the samples with 0.5 wt% NS properly dispersed than the same samples prepared by the literature mixing technique (See Figure 3-18). Portlandite was found less in the 0.5% new dispersion technique than in the 0.5% literature mixing technique which was 74 and 77%. The reduced amount of Portlandite shows that the NS particles are more active in the new mix than the literature mix due to the proper dispersion in the cement matrix. As the pozzolanic reaction will reduce the quantity of the Portlandite and transfer it to secondary C-S-H.

This high value of Portlandite recorded might be due to the fact that XRD only detect crystalline structure such as Portlandite presence in the samples. Thus, amorphous phases such as C-S-H cannot be detected and as such to have 100% total summation of the components in the samples, the quantity of crystalline phase is increased (Scrivener et al., 2004).

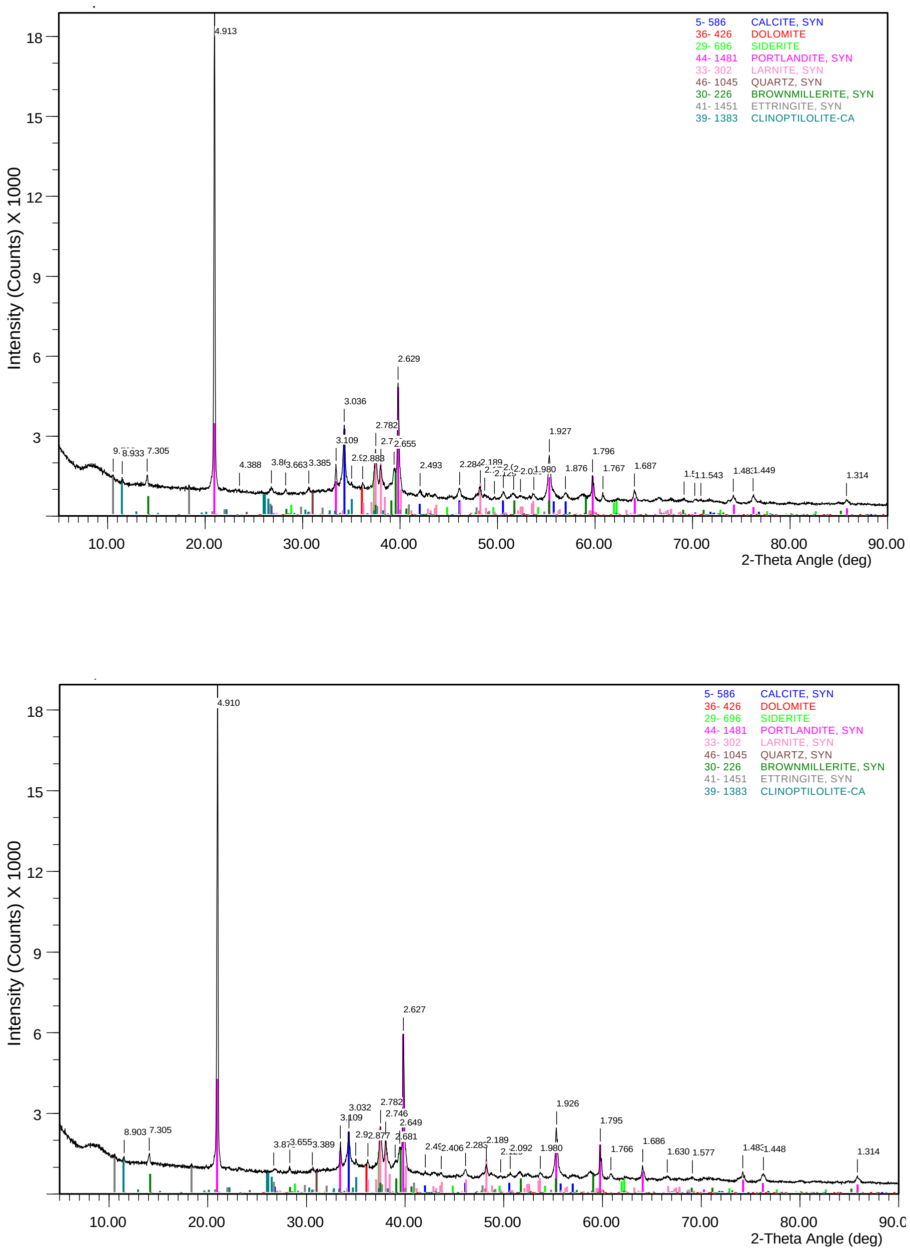


Figure 3-18: XRD analysis of 0.5 wt% NS samples prepared using literature (top) and new mixture technique (bottom) after 3 months of curing

3.7 SEM Analysis

SEM analysis was done to evaluate the structure of the Nano Silica based cement composites after curing it for 3 months as show in Figure 3-19. As it was shown earlier, the best results were obtained by 0.5 wt% NS cement sample prepared by the two different mixing methods. These samples were also cured under two different condition: 1) in a water bath under the temperature of 50°C and atmospheric pressure, 2) in the UCA chamber under the pressure and temperature of 50°C and 2200PSI for one day. These samples were then exposed to the ambient condition for 3 months.

The results obtained indicated that the new mixing method developed in this study gives a dense and smooth matrix to the cement compared to the conventional mixing method often reported in the literature. This could be due to the proper dispersion of Nano Silica in the cement matrix which increases its reactivity with Portlandite and creates well dispersed nucleation sites to facilitate the pozzolanic reaction.

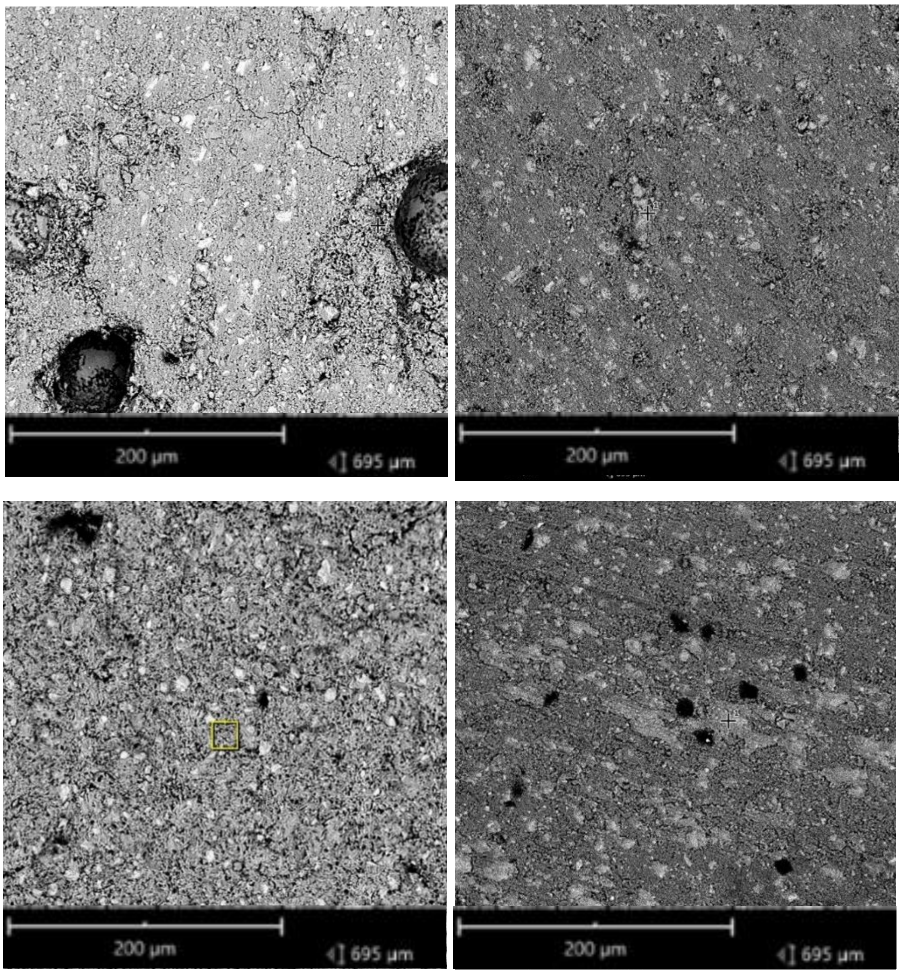


Figure 3-19: SEM analysis of 0.5 wt% Nano Silica-based cement after 3 months of curing: top left) literature mixing cured in the water bath, top right) new mixing cured in the water bath, bottom left) literature mixing cured in the UCA and bottom right) new mixing cured in the UCA

3.8 Discussions

There is no multiple reading of the rheological parameters in the studies carried out so far on the well cementing where the literature mixing was used to prepare the cement. There was also no indication as to whether the results presented are consistent once the tests are repeated. According to the results obtained from the measurements made on the samples prepared by the literature mixing approach, the rheological parameters of two samples with the same amount of Nano Silica are not similar and this discrepancy may cause a calamity in the field when the cement is prepared based on the laboratory recipe. The discrepancy in this case could be attributed to the poor dispersion of Nano Silica in the cement matrix, which may agglomerate and flocculate. This agglomeration is linked to the high surface area and presence of strong van der Waals forces. The proposed mixing method based on the sonication technique, however, was tested under different conditions where it was shown that the rheology of the cement is consistent once the tests are repeated. Having such consistency in the rheological behaviour is crucial to have a good estimation of the friction loss and pump horsepower for a safe cement job.

The compressive strength of the new mixing techniques-based samples was also higher than those of the literature mix. Although the difference between the strength of the samples cured under temperature and pressure of 50°C and 2200PSI seems to be only 200 psi, given the time period of the test which was only 8 hours, the results obtained are meaningful. This is because the cement sample achieves a higher compressive strength in a longer time period when the hydration of C_2S takes place in weeks or months. It was also revealed that although dispersions with different parameters may have different results, the compressive strength and many other parameters of the cement would be higher than the samples prepared by the literature mixing method. It was also found that regardless of the quantity of the Nano Silica replaced or the mixing technique used, the compressive strength of the cement composites is higher and their WOC is shorter compared to those of the neat cement. This is due to the fact that adding Nano Silica creates pozzolanic reactions through which SiO_2 reacts with Portlandite, producing secondary C-S-H, which is the main component contributing into the strength of the cement. This was further validated by the results obtained from the TGA and XRD which revealed that the quantity of $Ca(OH)_2$ decreases when Nano Silica is added. Moreover, a higher compressive strength and shorter WOC was given by the cement samples prepared by the new mixing technique. This could be due to the proper dispersion of Nano Silica in the cement, which gives more nucleation sites for the growth of C-S-H. However, careful analysis of the results highlighted that the optimum quantity of Nano Silica which could be replaced in the cement to have the highest strength and the lowest WOC is 0.75 wt%. This finding was aligned with the findings of previous studies carried out in recent years where it was indicated that above a certain quantity, Nano Silica does not contribute in the enhancement of the compressive strength (Kong et al., 2012; Kontoleontos et al., 2012; Kawashima et al., 2013). This could be due to: 1) agglomeration of nano particles, 2) variation of particle sizes in the cement slurry ranging from micro size of the cement to nano size of Nano Silica and 3) reduction of free water which hinders further hydration of the slurry, causing unhydrated grains to stop contributing into the strength development above a certain point (Rahman et al., 2015; Singh et al., 2016). Furthermore, from the SEM analysis, it was found that the samples cured under different conditions prepared with the new mixing technique gives a dense and smooth matrix to the cement compared to the samples prepared by the literature mixing technique.

From the TGA analysis point of view, it was concluded that adding Nano Silica into the slurry decreases the quantity of Portlandite due to the pozzolanic reaction, but it was not totally lost. It should be recalled that when the cement is exposed to wet/dry CO_2, Portlandite is initially attacked and is totally consumed before C-S-H being targeted, leading to the loss of the cement durability. Hence, it would be wise to reduce the quantity of Portlandite because it is a weak point in the cement matrix, but it should not be totally removed, as Portlandite slows down the carbonation rate when CO_2 reacts (Brandl et al., 2011; Ilesanmi, 2013).

To further emphasize on the importance of the dispersion method, dispersion parameters were changed and the compressive strength was recorded. The result highlighted that as the time and amplitude of the dispersion reduces, the agglomeration and flocculation of the Nano Silica take place which hinder the reactivity of pozzolanic reactions and reduce the compressive strength. Table 3-10 compares the advantageous of the new mixing technique presented in this study with those of the literature mixing method.

Table 3-10: Benefits of the new mixing technique over the literature mixing method

New Mixing Technique	Literature Mixture
Consistent rheological parameter	Inconsistent rheological parameters
Higher compressive strength	Lower compressive strength
Optimum quantity of NS came to be 0.75% with proper dispersion.	Optimum results achieve at 1 to 2%
Small amount of $Ca(OH)_2$ produces as the indication of pozzolanic reaction	$Ca(OH)_2$ did not significantly decrease as the indication of agglomeration and flocculation of NS in the cement
WOC decreases	WOC increases
Smooth and densified cement matrix	Rough cement matrix

3.9 Conclusions

In this chapter, different mixing techniques were applied and their effects on the rheological, morphological and strength parameters of the class G cement were examined. The optimum quantity of Nano Silica was highlighted for different mixing technique and it was found that a sophisticated mixing technique must be chosen once Nano Silica is added to the cement. It was found that the new mixing technique is able to give consistent rheological properties, short WOC, dense cement matrix and high compressive strength compared to the literature mixing. However, 1.5 wt% NS cement composite with the new mixing technique was discarded from this study because of its high viscosity. It was concluded that the optimum quantity of NS that can be replaced is 0.75 wt%. Moreover, it was found that changing the dispersion parameter such as amplitude and time may have significant impacts on the development of the compressive strength. Despite reduction in the compressive strength, 0.5 wt% Nano Silica based cement prepared with the changed dispersion parameter showed a higher compressive strength than the same sample prepared with literature mixing method. It should be noted that adding Nano Silica to the cement reduces the quantity of Portlandite in the samples due to the pozzolanic reactions, but it should not be totally removed as it slows down the carbonation rate.

Chapter 4: Application of Palm Oil Fuel Ash (POFA) in Oil Well Cementing

4.1 Introduction

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 study, attempts are made to show the application of Palm Oil Fuel Ash (POFA) as a supplementary cementing material (SCM) for drilling and completion practices. A series of experiments were conducted to evaluate changes in the density, free fluid, rheology, weight on cement, compressive strength, matrix structure and composition of the cement modified by POFA. Moreover, the effect of different curing condition on the hydration of the cement sample was evaluated by conducting TGA and determining the amount of Portlandite left in the sample.

Whereas, in the last part of this chapter a comprehensive comparison of NS and POFA based cement composite was given with respect to the different test conducted under the API standard. The quantitative and qualitative analysis of the NS and POFA cement composite was made with SEM and XRD analysis.

4.2 Methodology

4.2.1 Cement Compositions

Class G cement was considered for the purpose of this study as it is the commonly used cement in the oil industry. 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 in Sarawak Malaysia and was grounded for 8 hours in the ball mill to achieve the particle size of 12 microns. The physical and composition characteristics of POFA are given in Table 4-1 and Table 4-2 respectively.

Table 4-1: Physical Properties of Palm Oil Fuel Ash (POFA)

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 4-2: The XRF result reporting different oxides in the structure of POFA

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

4.3 Sample Preparation

The standard procedure followed for the preparation of the POFA based cement was American Petroleum Institute (API). This standard was chosen as it is commonly used in the petroleum industry for the preparation of primary and secondary cement. Moreover, different authors (e.g., Barlet-Gouedard et al., 2006, 2009; Kutchko et al., 2007, 2008; Garnier et al., 2010; Brandl et al., 2011; 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 are given in the API 10-A and 10-B.

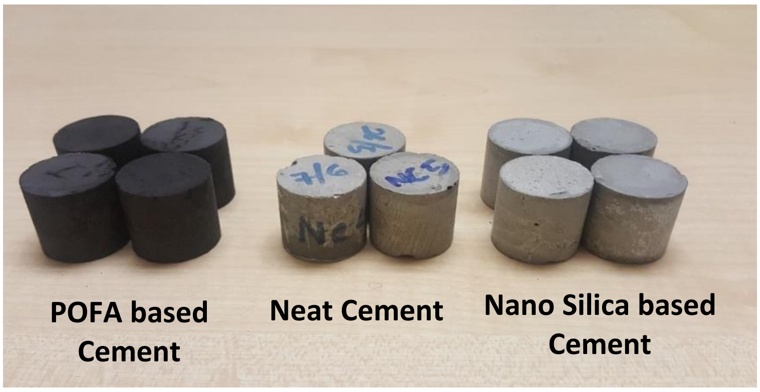


Figure 4-1: Different cement samples prepared for the purpose of this study

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 mix 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 with the class G cement. For the purpose of this study, the replacement of the cement with POFA ranged from 5 wt% to 20 wt% as given in Table 4-3. Figure 4-1 shows different cement samples prepared for the purpose of this study. It should be noted that Nano Silica based cement were also used in this study for the comparison purposes and their preparation technique is comprehensively presented in Chapter 3. Whereas, flow chart of the mixing of POFA with the Class G cement is shown in Figure 4-2.

Table 4-3: 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

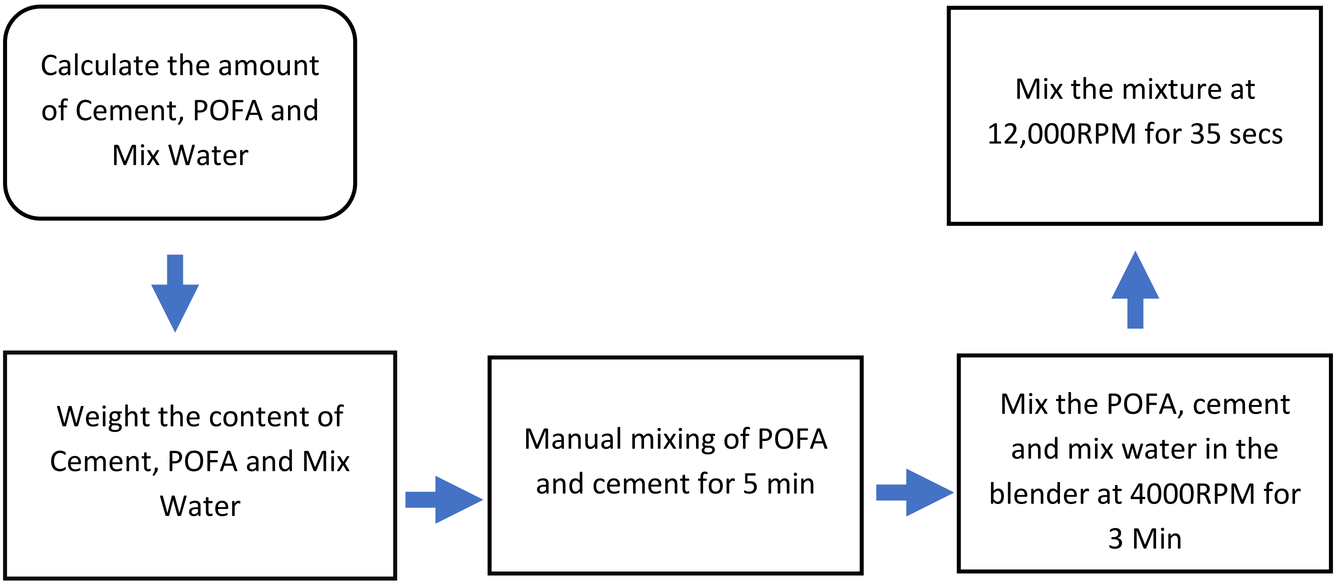


Figure 4-2: Flow chart of POFA cement composite mixing

4.4 Experimental Results

4.4.1 Density

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

Table 4-4: 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 samples except the one with 20 wt% POFA which has a lesser density than others. This could be due to the low density/specific gravity of POFA which cannot add extra weight once mixed with the Class G cement. This is mainly because the specific gravity of the grounded POFA varies from 2.05 to 2.78 whiles that of the class G cement is 3.15 (Khankhaje et al., 2016; Sooraj, 2013). For this study the specific gravity of POFA is 2.2 as described in Table 4-1. It was then concluded that POFA can also be used as an extender to reduce the density of the cement slurry in the intervals where lost circulation is encountered.

4.4.2 Free Fluid Test

Free Fluid test was conducted according to the API 10-A. 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:

$$FF = \frac{V_{ff} \times \rho}{m_s} \times 100 \tag{4-1}$$

where FF is the free fluid content, V_{ff} is the volume of supernatant fluid collected, ρ is the specific gravity of the slurry and m_s is the mass transferred to the conical flask. By using this equation, the free fluid percentage of the POFA based cement was obtained and summarised in Table 4-5. Figure 4-3 shows the collection of supernatant fluid as part of the free fluid test.

Table 4-5: Percentage of free fluid in the POFA cement composites

POFA Content (%)	Mass Transferred (g)	Specific Gravity	Volume of Supernatant fluid (ml)	Free Fluid (%)
0	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

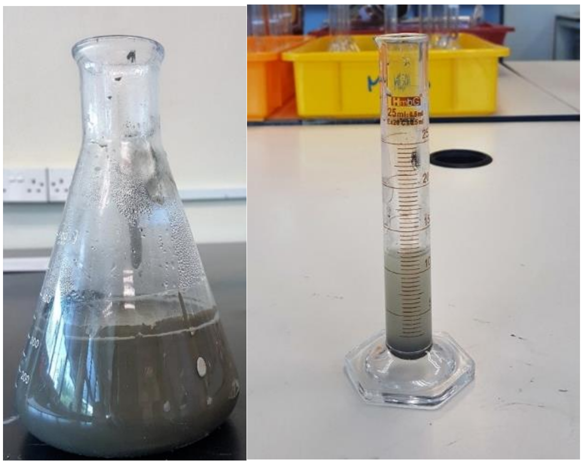


Figure 4-3: Collection of supernatant fluid for the free fluid test

Summarised in Table 4-5, 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 in the cement slurry. However, all POFA cement composites passes the threshold limit stated in the API 10-A which emphasis 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 defined by the viscosity of the cement designed.

4.4.3 Rheology

Rheology of the cement is an important parameter indicating the horse power required and the frictional loss induced during the cement placement. Two commonly used mathematical models in the petroleum industry for determination of the rheological behaviour of the cement are Power law and Bingham plastic. Among these two, 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 indicate the apparent viscosity and the degree of the non-Newtonian behaviour in the cement slurry. Whereas, for the measurement of n and k for the power law, a log log graph was plot between the shear stress (Pa) and shear rate (1/s) for the purpose of achieving a straight-line equation in which n is represented by the slope and k by the intercept

For determination of the rheological behaviour of the POFA based cement, the API 10-B guideline 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 unfavourable changes the cement properties. The results obtained from the rheological measurements of the POFA based cement are summarised in Figure 4-4, Figure 4-5 and Table 4-6. It should be noted that each test was repeated twice for the same cement composition to ensure the consistency of the results.

Table 4-6: Plastic viscosity and yield point of POFA cement composite

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	8.17
10	128.46	34.50	0.45	10.16
15	118.12	35.35	0.42	11.48
20(a)	124.58	34.03	0.46	9.16
20(b)	127.8	36.03	0.44	10.57

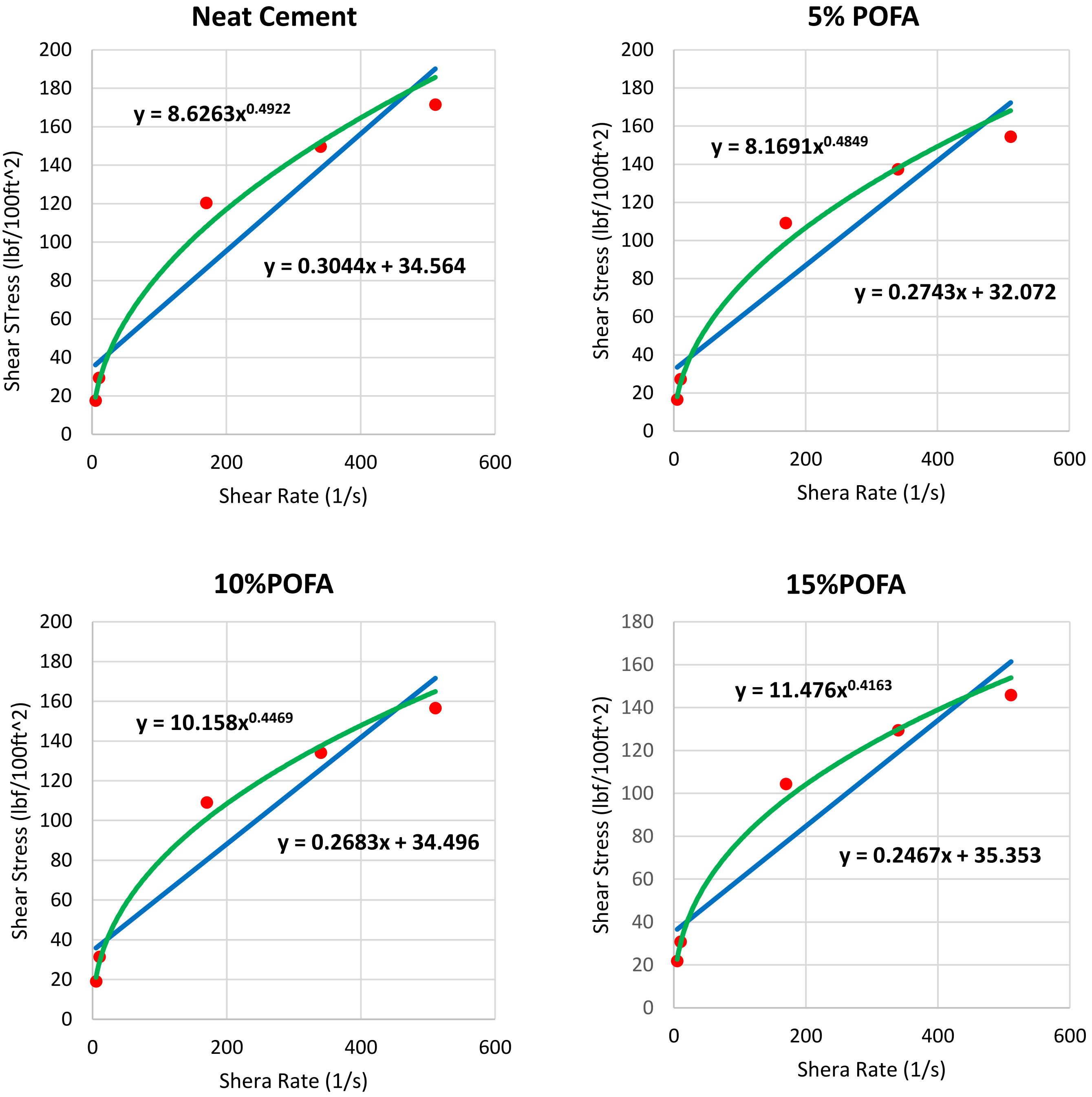


Figure 4-4: Flow curve of the neat cement and POFA based cement composites described by the Power-law and Bingham Plastic models

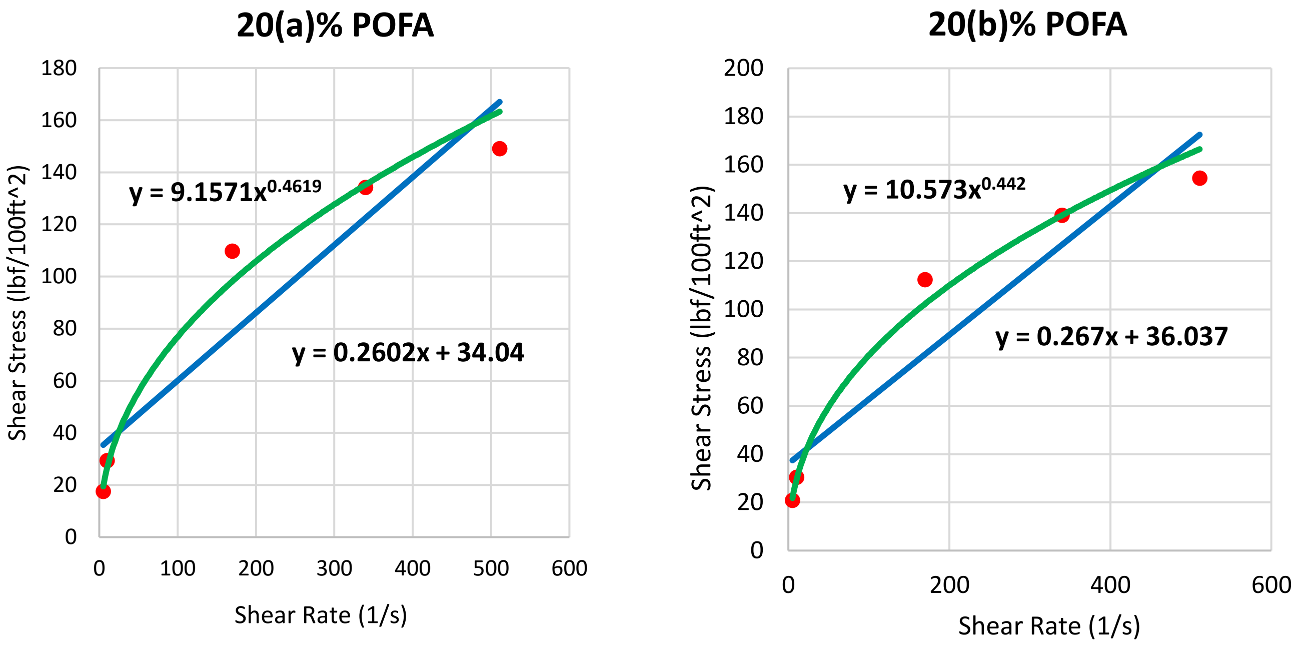


Figure 4-5: Comparison between the rheological behavior of two cement composites with 20 wt% POFA

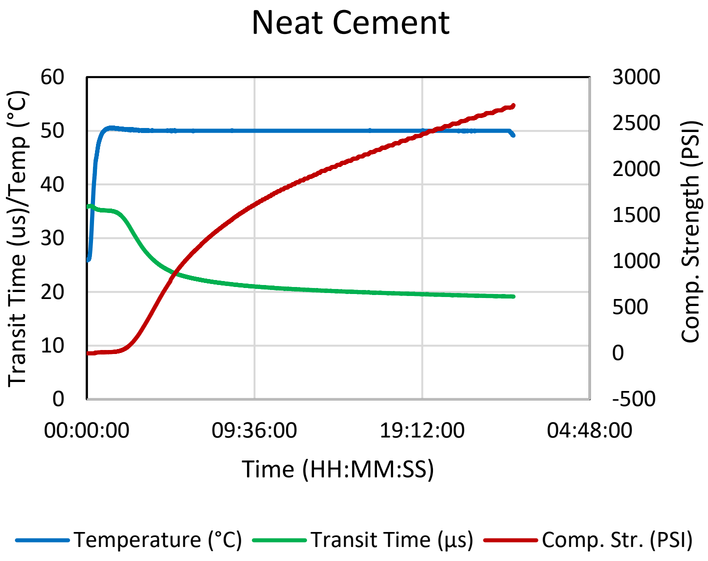
The rheological measurements of the POFA based cement highlighted that the plastic viscosity and the yield point of the neat cement is higher than all POFA based cement composites. The decrease in the rheological properties of the samples could be linked to the fact the POFA is a pozzolanic material 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.

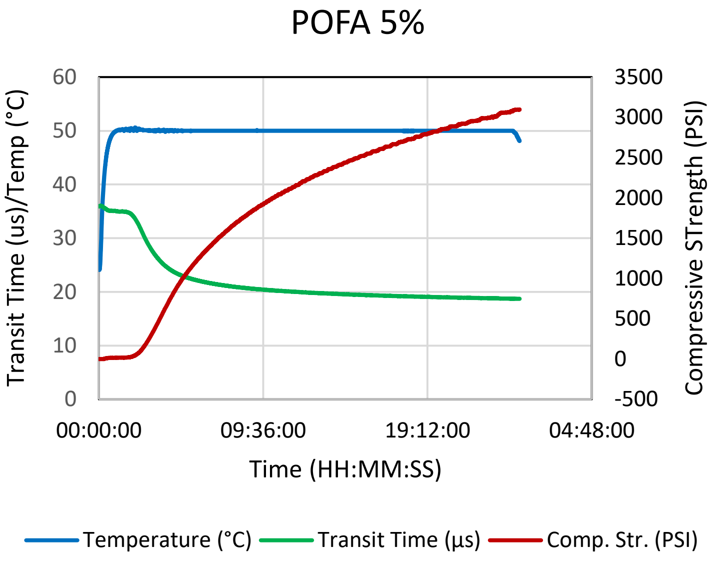
4.4.4 Compressive Strength

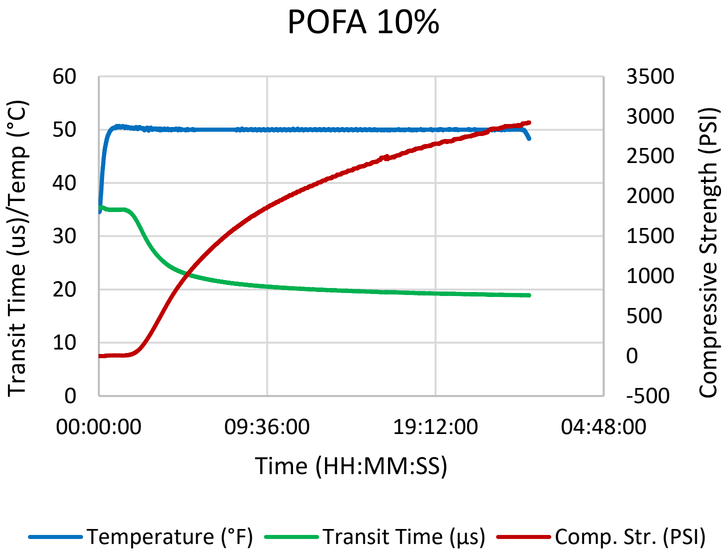
4.4.4.1 Non-Destructive Test

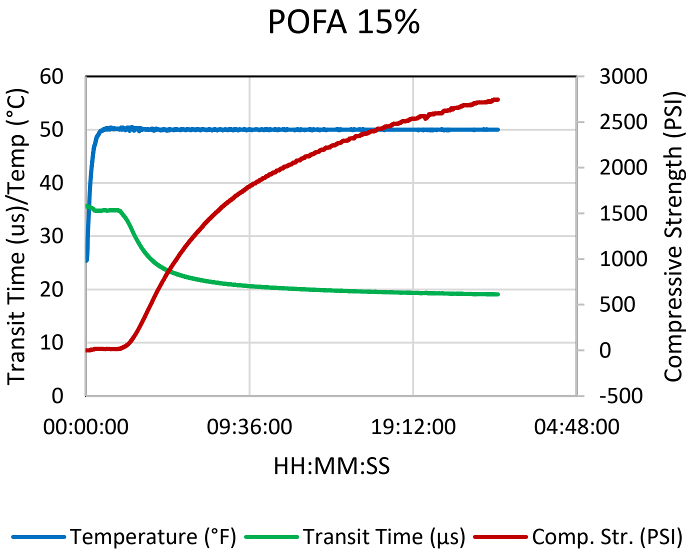
Compressive strength is an important parameter in the cement design which indicates the maximum load sustained by any materials before failure. For determination of the compressive strength in real time, Fann Ultrasonic Cement Analyser (UCA) Eurotherm Model

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 before starting the next phase of drilling). The tests were carried out for 24 hours at the temperature and pressure of 50°C and 2200PSI (15MPa) respectively for different POFA cement composites. The results obtained are shown in Figure 4-6 and Table 4-7.


Neat Cement


POFA 5%


POFA 10%


POFA 15%

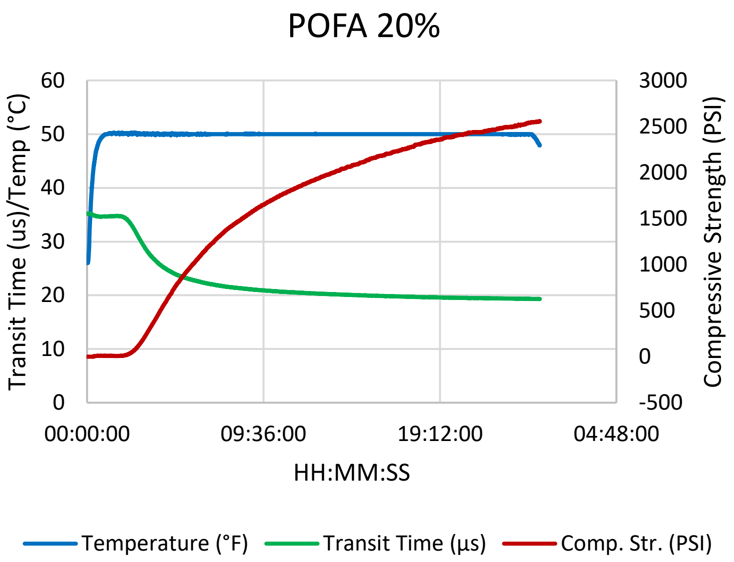


Figure 4-6: Compressive strength of different POFA cement composites obtained from UCA

Table 4-7: 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 20 wt% POFA. However, it was found 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 4-8: WOC for the POFA based cement composite

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

The result of WOC is shown in Table 4-8 which indicated 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 20min difference between the WOC of 5 wt% POFA with that of the neat cement which can reduce the Non-Productive Time (NPV) significantly.

4.4.4.2 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. The curing was done at the temperature of 50°C and 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 POFA based cement were recorded as shown in Figure 4-7. The destructive test was not conducted on the 20 wt% POFA based cement due to its low compressive strength development recorded by UCA after 24 hours.

It was found that 5 wt% POFA based cement has a higher compressive strength than 10 wt% and 15 wt% POFA based cement respectively. It was also found that the compressive strength of the POFA based cement 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 further 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.

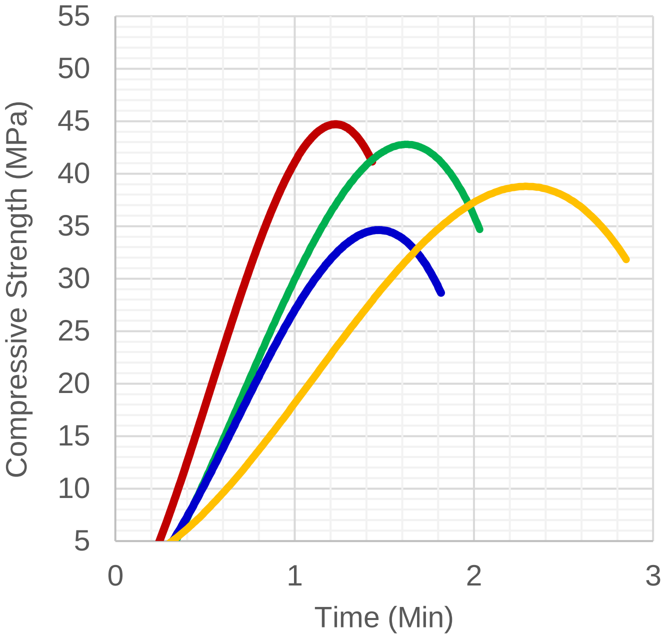


Figure 4-7: Stress-time curves showing the compressive Strength of neat (yellow), 5 wt% POFA (maroon), 10 wt% POFA (green), 15 wt% POFA (blue) based cement

4.4.5 Thermogravimetric Analysis

Characterization of the POFA 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 characterization of the POFA based cement, the weight loss due to 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 sample. 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 sample, the following equation was used (Jain and Neithalath, 2009; Lim and Mondal, 2015):

$$CH (\%) = WL_{(CH)} (\%) * MW_{(CH)}/MW_{(H)} \qquad (4-2)$$

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, cement samples exposed to the downhole condition in the UCA were chosen. It was found that the least amount of Portlandite left in the samples belongs to 5 wt% POFA based cement samples. The TGA results of the samples after 1 day of curing in the UCA are shown in the top left side of Figure 4-8 and summarised in Table 4-9.

Table 4-9: Percentage of Portlandite left in the sample after 1 day of curing in UCA

POFA Content (%)	Weight loss (%)	Portlandite (%)
0 (Neat Cement)	2.8716	11.80
5	2.1273	8.743
10	2.2464	9.233
20	1.829	7.51

From Table 4-9, it can be concluded that the least amount of Portlandite was in the 20 wt% POFA based cement due to the significant amount of cement replacement. Neglecting the results obtained from 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 found that the compressive strength of 5% 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 which produces secondary C-S-H.

4.4.5.1 Curing Age

To further assess the best cement composition, TGA was done on 5 wt% POFA based cement cured under similar conditions for 1 day and 1 month. The results obtained indicated that the weight loss after one month of curing is 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 pozzolanic reaction takes place due to the presence of POFA. To further confirm these results, one more test was done on the 10% POFA cement and a similar result was observed when 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 4-8.

4.4.5.2 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 of neat cement 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. 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 in the top right side of Figure 4-8.

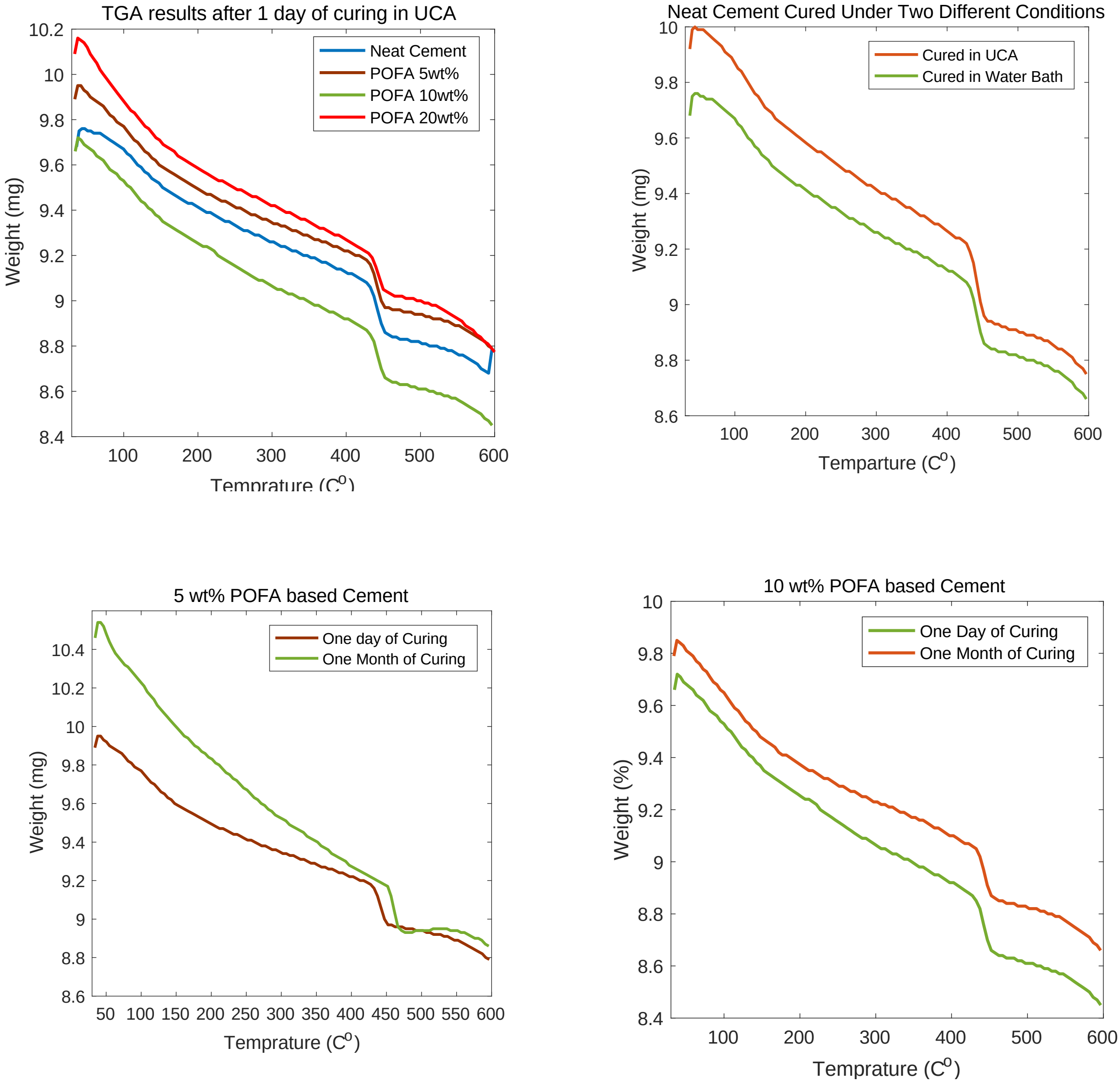
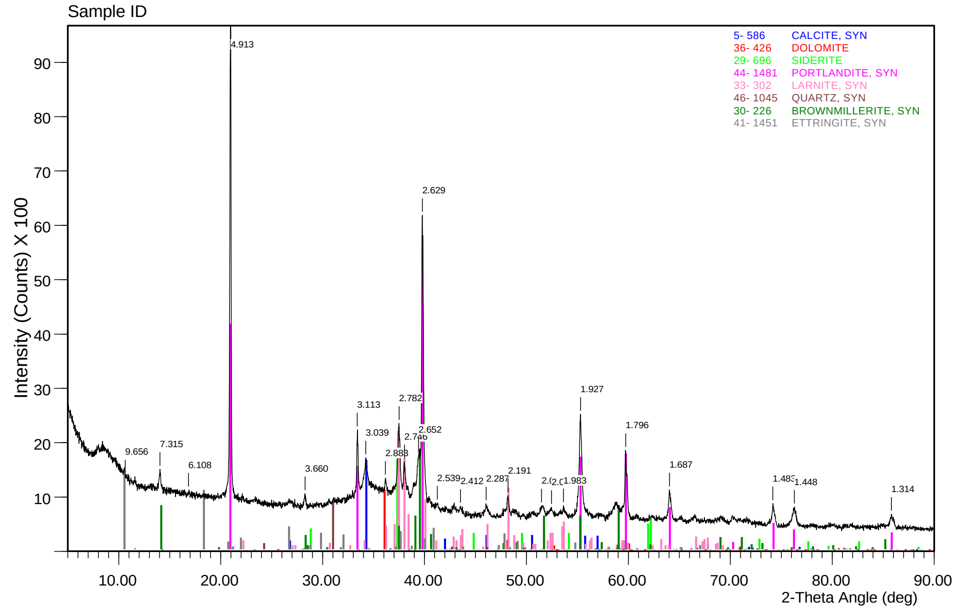


Figure 4-8: Weight loss in the cement under different curing conditions obtained from TGA

From the TGA analysis it was found that the amount of Portlandite left in the neat sample cured in the UCA had a higher amount of Portlandite left i.e. 11.80% whereas the sample in water bath produced only 10.07% of Portlandite. 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.

4.4.6 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 Portlandite was in 20 wt% POFA based cement which was mainly because of the high replacement level. The results obtained from the XRD analysis are shown in Figure 4-9 and summarised in Table 4-10. It should be noted that the high value of Portlandite observed in the Table 4-10 is due to the fact that XRD analysis can only detect crystalline (Portlandite) phases not the amorphous phases such as C-S-H.



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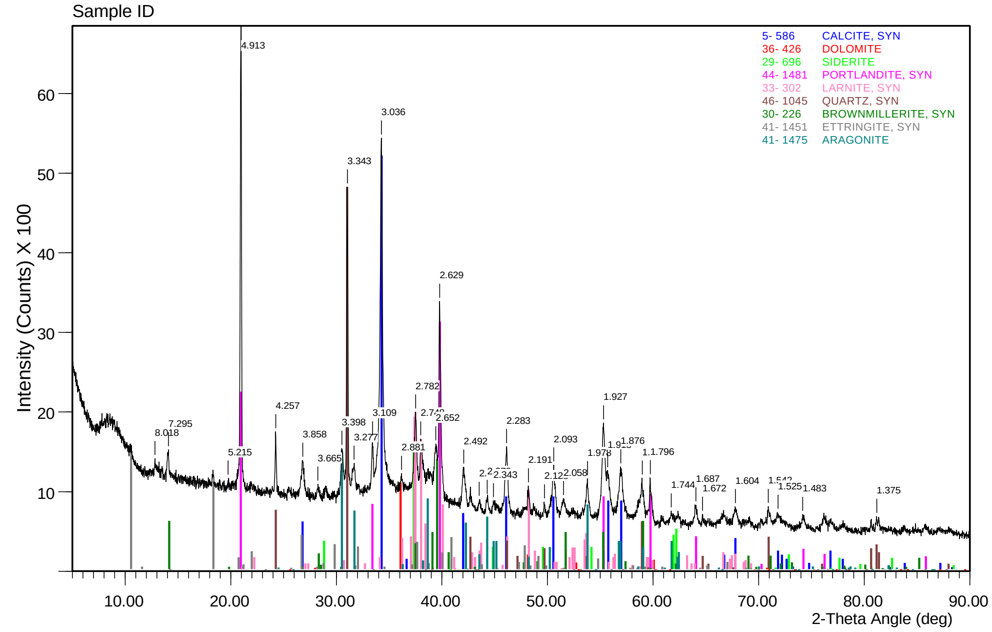

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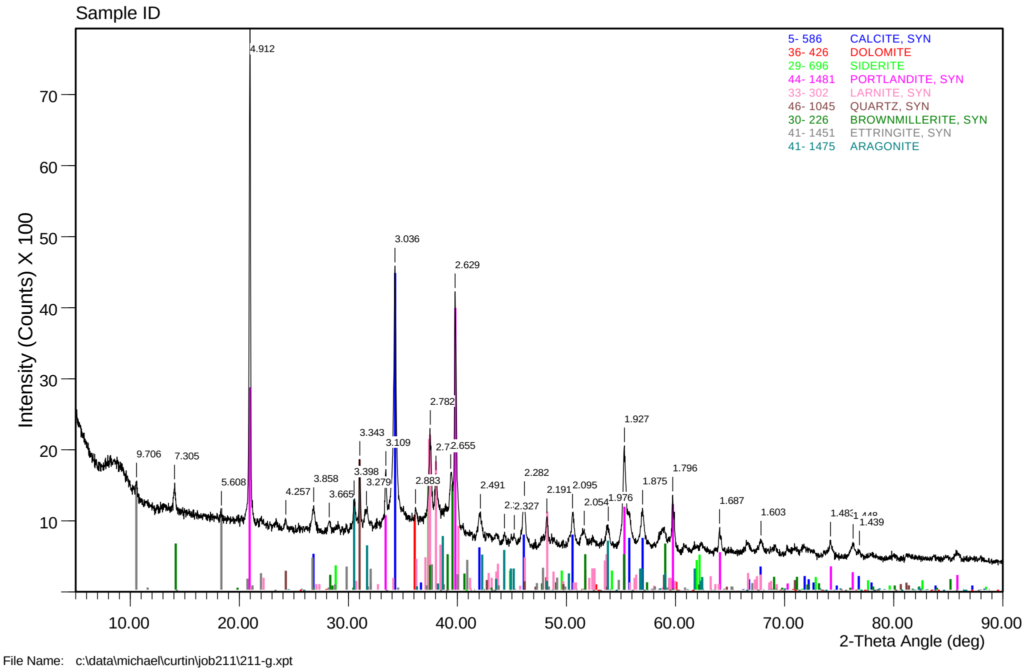


Figure 4-9: From top: XRD analysis of neat, 5 wt% and 20 wt% POFA based cement after 6 months of curing

Table 4-10: 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

4.4.7 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 4-10, indicated that the cement with 5 wt% POFA has a more densified and smoother surface compared to 20wt% POFA based cement.

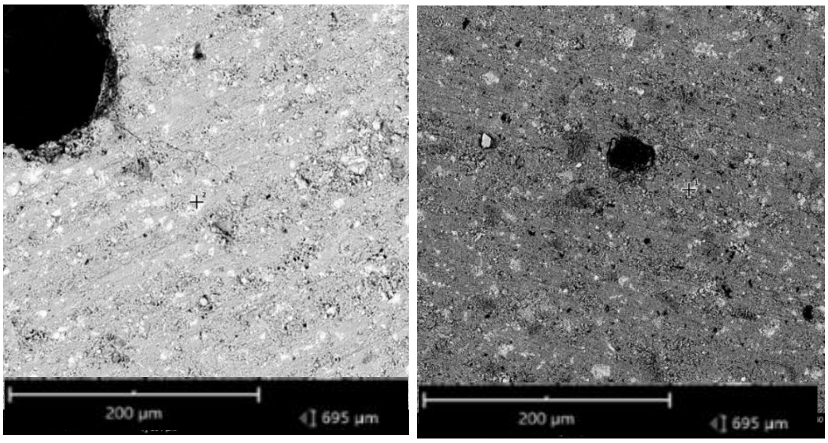


Figure 4-10: SEM analysis of 5% POFA cement composite (left) and 20% POFA cement composite on the right

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 4-11.

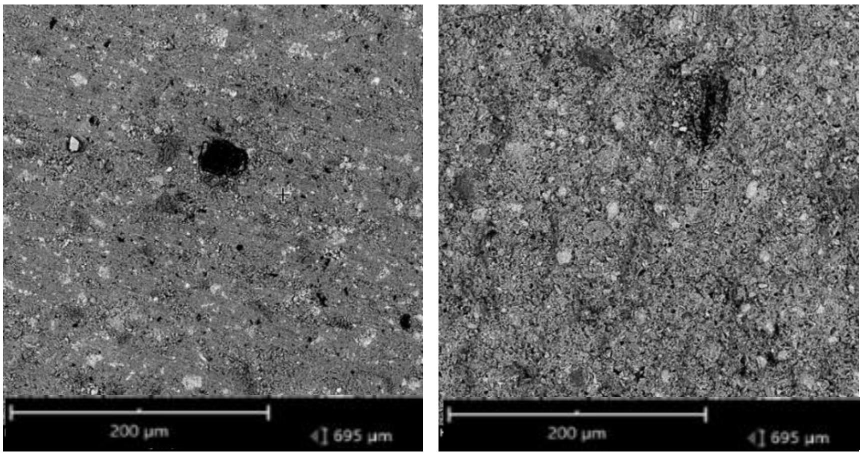


Figure 4-11: SEM of 20 wt% POFA based cement cured in the UCA (left) and water bath (right)

Looking at Figure 4-11, 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 good efficiency of POFA based cement observed through different tests, attempts were made to compare its performance with Nano Silica based cement which is known as one of the best cement in terms of compressive strength and physical properties (Abid et al., 2017). This comparison is provided and discussed in the next section.

4.5 Nano Silica 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, Nano Silica 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 Nano Silica based cement samples used in this study were prepared according to the new mixing (sonication dispersion) method presented in Chapter 3. As such, the preparation procedure of the samples is not discussed in this chapter.

4.5.1 Density

Measurements of the density of the samples were done using the same procedure presented earlier with the results reported in Table 4-11. According to this table, there is not that much of difference between the density of the POFA and NS based cement with that of the neat cement.

Table 4-11: 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 Nano Silica 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.

4.5.2 Rheology

The plastic viscosity and the yield point of the Nano Silica based cement were determined using the Bingham law and compared with those of the POFA based cement as reported in Table 4-12.

Table 4-12: Rheological properties comparison between the NS and POFA cement composites

NS (POFA) Content (%BWOC)	Plastic Viscosity of NS cement (cP)	Plastic Viscosity of 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 4-12, it can be seen that adding more than 1 wt% Nano Silica will increase the plastic viscosity of the cement even higher than that of the neat cement, which may not be favourable. Unlike Nano Silica, the POFA based cement provided a lower plastic viscosity compared to the neat cement. An opposite trend was observed for the POFA and Nano Silica based cement in terms of rheological changes. This discrepancy might be related to the particle size since the size of Nano Silica used in this study was between 15 to 20 nm whilst that of POFA was 12 microns. Therefore, Nano Silica has a higher surface area and is much more reactive than POFA. It should also be recalled that Nano Silica is more hydrophilic than POFA and will absorb more free water, which ultimately increases the plastic viscosity of the cement.

4.5.3 Compressive Strength

The compressive strength of the cement bearing POFA and Nano Silica was determined using the UCA machine. The measurement was done for 24 hours at the temperature of 50°C and pressure of 2200PSI. Table 4-13 and Figure 4-12 compares the compressive strength development in the POFA and Nano Silica based cement.

From Table 4-13 and Figure 4-12, it is seen that the best compressive strength belongs to 0.5% Nano Silica based cement (i.e., 3019.82 psi) followed by 5 wt% POFA based cement (i.e., 2919.73 psi) with the difference of 100 psi. It was interesting to see that unlike POFA based cement, the compressive strength of Nano Silica based cement increases as the amount of Nano Silica increases. However, this trend starts to decline after adding more than 0.5 wt% Nano Silica. This decrease in the compressive strength of Nano Silica based cement 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 replacement.

Table 4-13: Compressive strength of POFA and Nano Silica based cement after 24 hours of curing

Hours	Neat Cement	5% POFA (PSI)	10% POFA (PSI)	15% POFA (PSI)	20% POFA (PSI)	0.25% NS (PSI)	0.50% NS (PSI)	0.75% NS (PSI)	1% NS (PSI)
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

In the next stage, it was attempted to evaluate the strength of the cement after nine months of curing through destructive tests. The results obtained are given in Table 4-14 and shown in Figure 4-13.

The destructive test on the Nano Silica and POFA based cement cured for the time period of 9 months revealed that the highest strength is achieved by 5 wt% POFA based cement whilst the highest strength of Nano Silica based cement was achieved by the one having 0.75% Nano Silica. 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 reaction with silica but as the aging continues, hydration of C_2S and C_3S produces Portlandite and enhances the pozzolanic reaction.

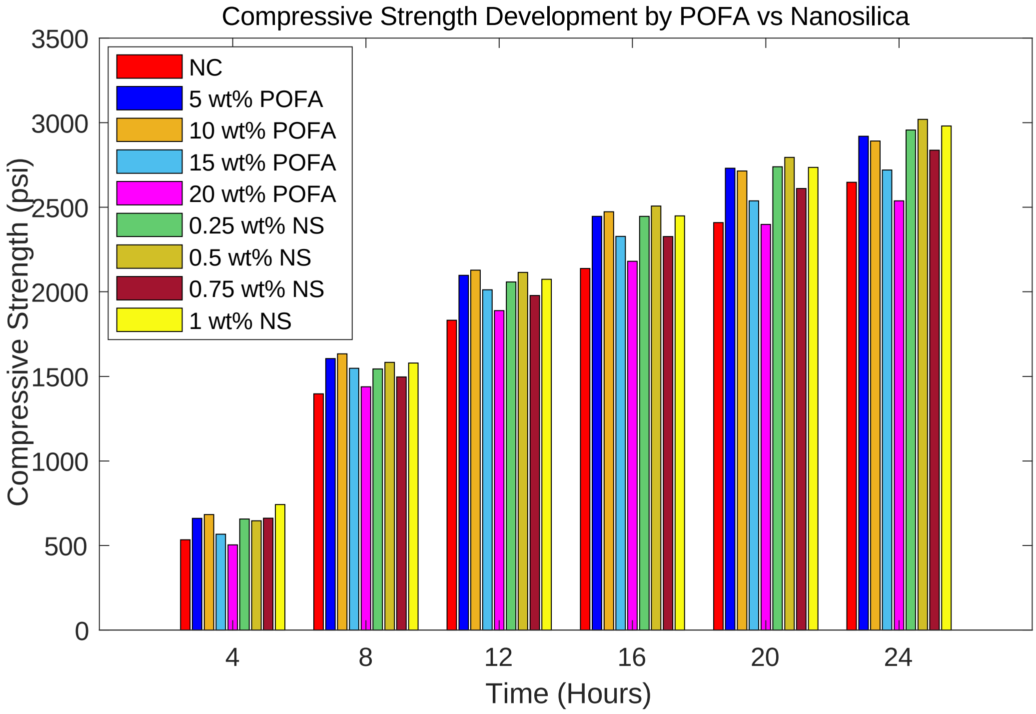


Figure 4-12: Compressive strength of NS and POFA based cement after 24 hours of curing

Table 4-14: 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

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, Nano Silica acts as an accelerator in the development of the compressive strength. These behaviours of the cement in the strength development could also be related to the replacement level of Nano Silica and POFA. In fact, POFA had a higher replacement level then

Nano Silica 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 the replacement level beyond a certain threshold will saturate the cement slurry and the strength decreases when POFA or any other pozzolanic materials are added.

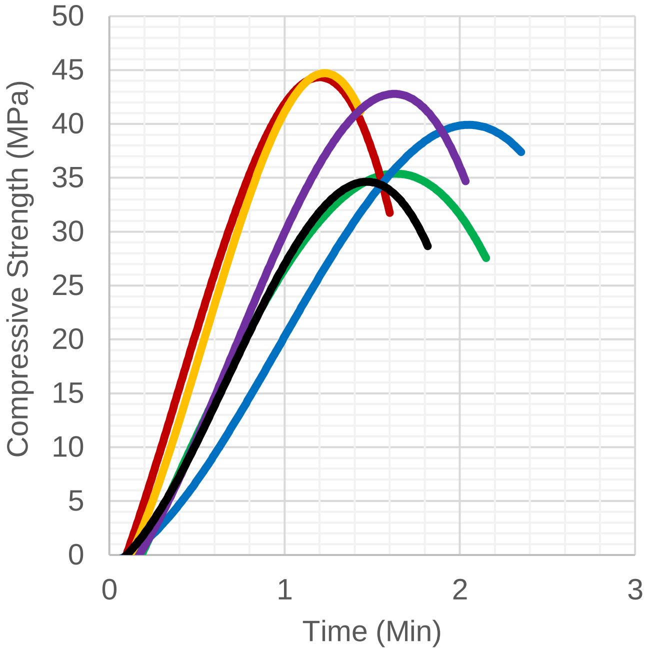


Figure 4-13: Stress-time curves showing the compressive Strength of 5 wt% POFA (yellow), 10 wt% POFA (purple), 20 wt% POFA (black), 0.25 wt% NS (green), 1 wt% NS (blue), 0.75 wt% NS (maroon) based cement

4.5.4 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% Nano Silica 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 sample was also calculated from the Eq (4-2). The test was performed on the samples cured for 24 hours at the pressure of 2200PSI and the temperature of 50°C. The result obtained are given in Table 4-15.

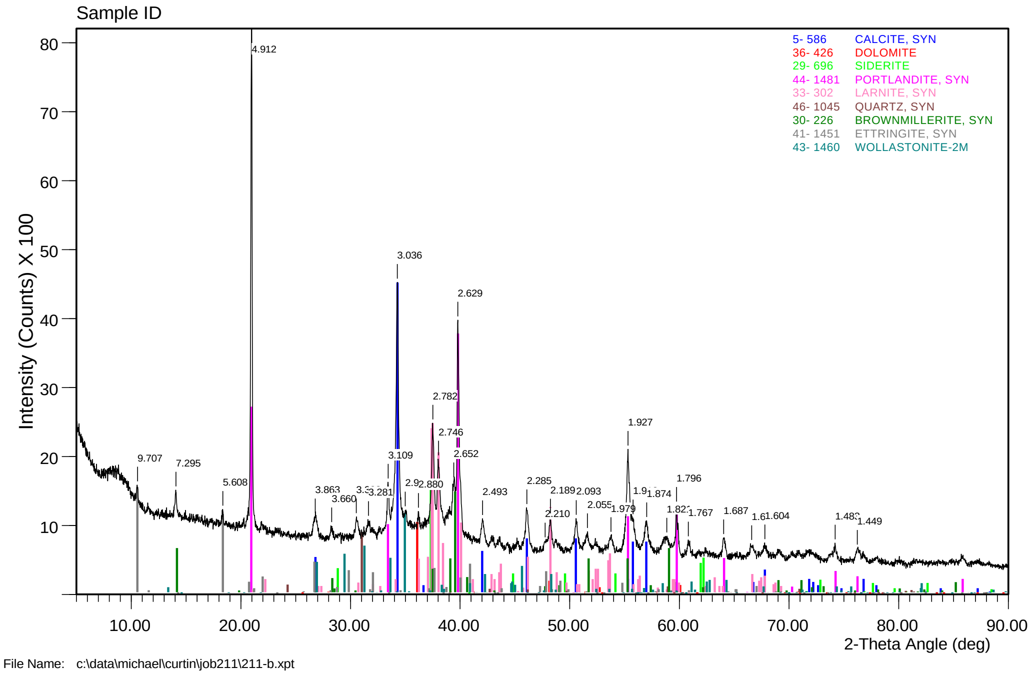
Table 4-15: The results obtained from performing TGA tests on 0.5 wt% NS and 5% POFA based cement

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 this Table, a lesser amount of Portlandite is left in the POFA based cement compared to the Nano Silica's. However, the percentage difference between these two samples was only 10.9%. Considering the fact that only 0.5 wt% Nano Silica was added to the cement, it seems that Nano Silica is much active/reactive pozzolanic material than POFA.

4.5.5 XRD Analysis

Choosing two cement samples from each category as the best and representative samples, XRD analysis was only done on 0.5 wt% Nano Silica 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 4-14 and Table 4-16.



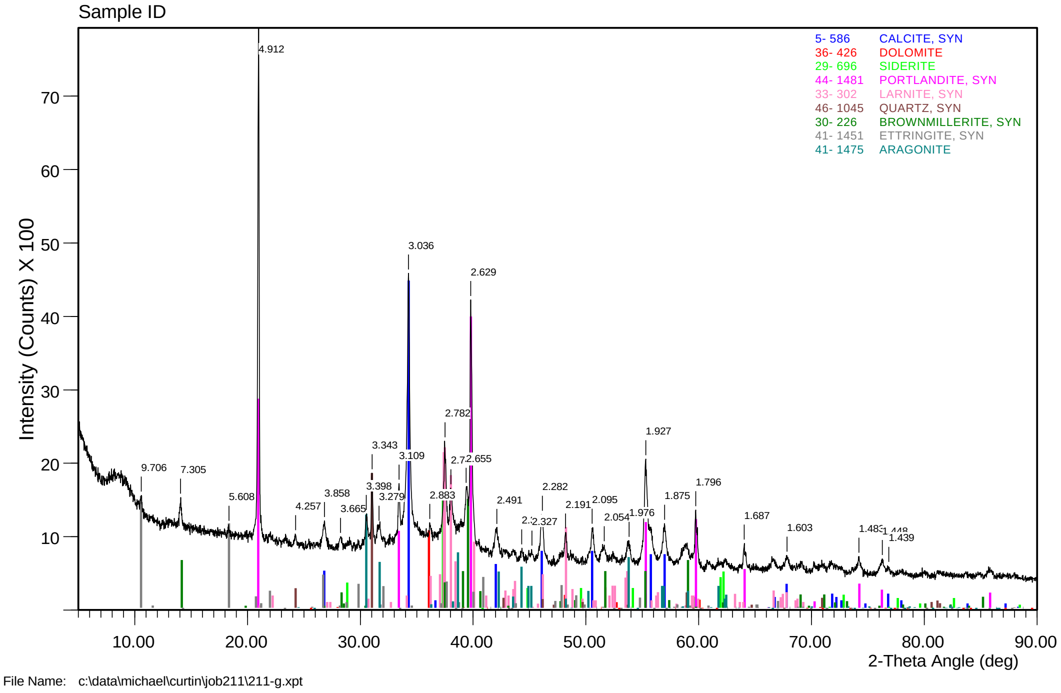


Figure 4-14: XRD analysis of 0.5 wt% Nano Silica (top) and 5 wt% POFA (bottom) cement

Table 4-16: Amount of Portlandite left in the sample after 6 months of curing

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

From the result reported in Table 4-16, one can conclude that the least amount of Portlandite is present in the 5 wt% POFA based cement due to the fact that the continuous reactivity of POFA with Portlandite occurs long after the initial curing. That is the main reason why the highest compressive strength was produced by 5 wt% POFA based cement after 9 months of curing.

4.5.6 SEM Analysis

SEM analysis was done to evaluate the structure of the Nano Silica and POFA based cement after curing. It can be seen from the Figure 4-15 that more dense and compacted cement matrix was achieved by the 0.5% NS cement composite. This is due to the fact that the Nano Silica have large surface area that will increase the reactivity of Nano Silica with Portlandite. Moreover, due to its nano size more nucleation sites will be generated in the cement structure that will reduce the porosity and permeability of the cement and will give a compacted cemented matrix

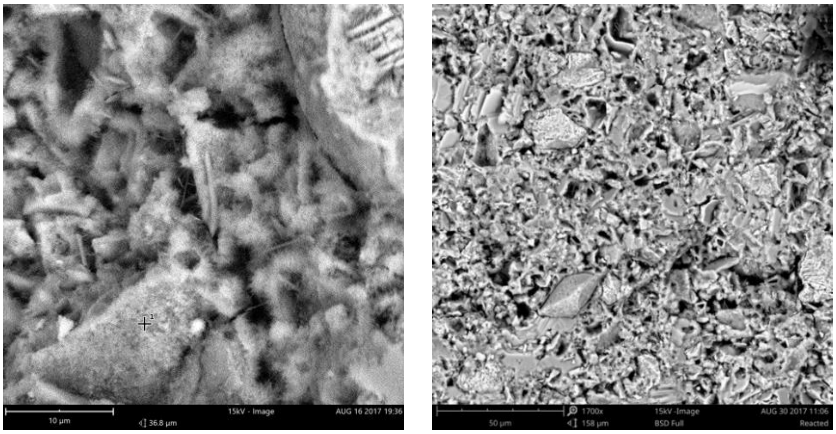


Figure 4-15: Structure of the POFA based (left) and Nano Silica based (right) cement

4.6 Discussion

There have been many studies to improve the cement sheath integrity exposed to different pressure and temperature conditions. It seems that the density of the POFA based cement 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 Nano Silica 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 to as much as that of the Nano Silica based cement and acting as a retarder are perhaps the best features of POFA which could not be observed in the cement mixed by Nano Silica. 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 surface 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 strength development in the cement continues months after placement, POFA, as a cheap additive which does not need any dispersion for the cement preparation, could be a good option as a SCM in the oil well cementing industry.

4.7 Conclusion

In this study, the application of POFA, as an agricultural waste, in the oil well cementing was evaluated and compared with the Nano Silica 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 Nano Silica, 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.

Chapter 5: Rice Husk Ash as the Partial Replacement in the Class G Cement

5.1 Introduction

In this chapter, the effect of Rice Husk Ash (RHA) on class G cement is evaluated. A series of experiments were conducted on the RHA based cement including density, free fluid, compressive strength (destructive and non-destructive) and TGA tests that are discussed. The main purpose of using RHA in this thesis was to provide a deeper insight into the application of agricultural wastes in the petroleum and cement industries. It should be noted that RHA is known as a potential pozzolanic material and has shown successful application in the concrete industry. The cement samples prepared by adding RHA in the study were also subjected to the carbonation test but the results obtained will be discussed in the next chapter.

5.2 Methodology

5.2.1 Cement Composition

The cement used in this chapter was the same Class G cement used earlier to prepare Nano Silica and POFA based samples. RHA was bought from the Llh Biomass SDN BHD which was burned at the temperature of 400 to 600°C for 4 to 6 hours. Before mixing and sample preparation, RHA was grounded and sieved through a 75-micron mesh. The results obtained from performing the XRF tests on RHA is given in Table 5-1 and Table 5-2.

Table 5-1: Element analysis of the RHA obtained from the XRF test

No.	Element	Percentage
1.	Silicon (Si)	83.43
2.	Potassium (K)	9.26
3.	Phosphorous (P)	2.64
4.	Calcium (Ca)	2.32
5.	Chlorine (Cl)	1.11
6.	Iron (Fe)	0.34
7.	Sulphur (S)	0.31
8.	Manganese (Mg)	0.30
11.	Copper (Cu)	0.02

Table 5-2: Oxide groups present in the structure of RHA obtained from the XRF test

No.	**Oxide**	**Result**	**Unit**
1.	Silicon Dioxide (SiO_2)	92.02	%
2.	Potassium Oxide (K_2O)	3.70	%
3.	Phosphorous Oxide (P_2O_5)	1.97	%
4.	Calcium Oxide (CaO)	1.06	%
5.	Chlorine (Cl)	0.40	%
6.	Sulphur Trioxide (SO_3)	0.25	%
7.	Magnesium Oxide (MgO)	0.23	%
8.	Iron Oxide (Fe_2O_3)	0.15	%
9.	Manganese Oxide (MnO)	0.11	%
10.	Aluminium Oxide (Al_2O_3)	0.10	%
11.	Zinc Oxide (ZnO)	0.01	%
12.	Copper Oxide (CuO)	70	ppm
13.	Rubidium Oxide (Rb_2O)	59	ppm
14	Strontium Oxide (SrO)	34	ppm

5.2.2 Sample Preparation

For the preparation of the cement samples, the standard practices presented by API (American Petroleum Institute) were followed. This standard was chosen as it is the most widely used standard in the petroleum industry. Moreover, many studies carried out on the well cement used the API standard for preparation, mixing and testing procedures (Barlet-Gouedard et al., 2006; Barlet-Gouédard et al., 2007; Kutchko et al., 2007; Kutchko et al., 2008; Garnier et al., 2010; Brandl et al., 2011; Lesti et al., 2013; Zhang et al., 2014).

Mixing of RHA with the cement was done following the same process used to prepare the POFA based cement as described in Chapter 4. The flow chart showing the mixing procedure of RHA with the cement is shown in Figure 5-1. RHA replacement in the cement was from 1 to 5 wt%, although the replacement level of RHA in the concrete industry is more than 5wt%. This was mainly because any replacement above 5 wt% would need superplasticizer to increase the workability or to reduce the rheological properties of the cement/concrete (Thomas, 2018). This could cause difficulty in understanding the effect of RHA since superplasticizer could induce changes in the physical and mechanical properties of the cement. The composition of the cement used in the study is given in the Table 5-3.

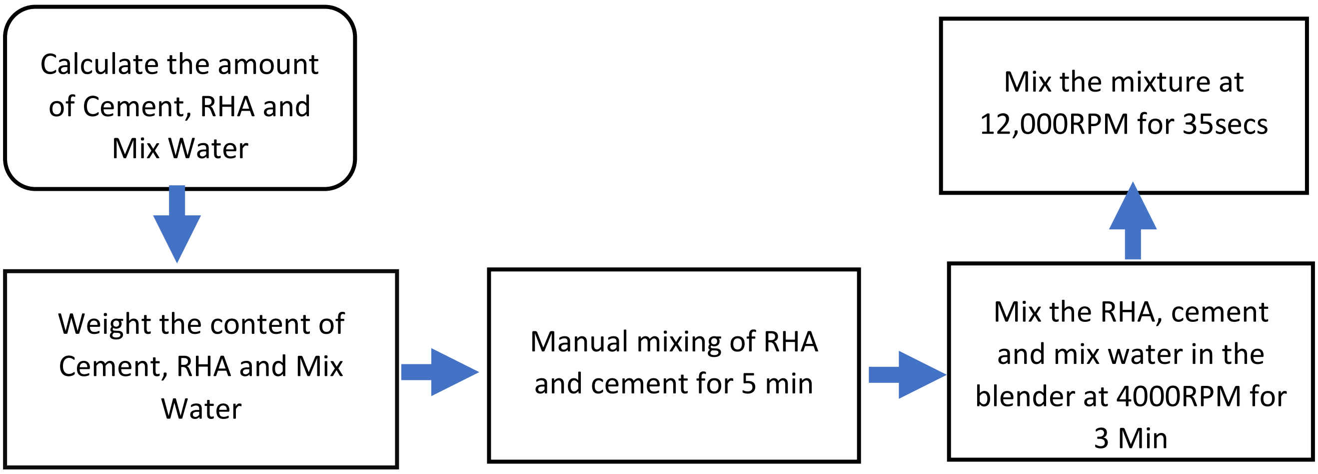


Figure 5-1: Flow chart of RHA cement composite mixing

Table 5-3: Different RHA based cement used for the purpose of this study

Sample No.	Content of RHA (%)	Weight of RHA (g)	Weight of Cement (g)	Mix water (g)
1	0	0	692	305
2	1	6.92	685.08	305
3	2	13.84	678.16	305
4	3	20.76	671.24	305
5	4	27.68	664.32	305
6	5	34.6	657.4	305

5.3 Experimental Results

5.3.1 Density

Density is one of the important parameters in the cement design which determines the amount of pressure applied on the formations during placement. The density of the samples was measured using the Fann Mud Balance TruWate Model 141. The density and the specific gravity of the RHA based cement is shown in Table 5-4.

Table 5-4: Density and specific gravity of RHA based cement

RHA content % (BWOC)	Density (ppg)	Specific Gravity
0	15.3	1.84
1	15.45	1.85
2	15.35	1.84
3	15.3	1.84
4	15.05	1.81
5	15.1	1.81

From Table 5-4, it can be seen that the density of the RHA based cement remained the same as that of the neat cement. The reason for the consistent density is linked to the fact that a very small amount of RHA had replaced the cement. However, for the replacement level above 3 wt%, a slight drop in the density of the samples was observed because the specific gravity of RHA (2.05 to 2.53) is less than that of the Portland cement (3.10 to 3.14) (Rukzon and Chindaprasirt, 2009; Christopher et al., 2017).

5.3.2 Free Fluid Test

For the measurement of the free fluid test, the API standard 10-A was followed. The procedure of the test was similar to the method presented in the previous chapter for the POFA based cement. Table 5-5 summarizes the percentage of free fluid collected from the samples.

Table 5-5: Percentage of free fluid in the RHA cement composites

RHA Content (%)	Mass Transferred (g)	Specific Gravity	Volume of Supernatant fluid (ml)	Free Fluid (%)
0	763.3	1.84	11.5	2.77
1	762.53	1.85	7	1.70
2	762.51	1.84	7	1.69
3	763.35	1.84	6	1.45
4	762.8	1.81	6	1.42
5	762.61	1.81	5	1.19

As it seen in Table 5-5, as the quantity of RHA in the cement increases, %FF decreases. To be precise, the percentage difference of free water between the neat cement and 5 wt% RHA based cement is around 80%. This is due to the high specific area of RHA which is linked to its honey comb like structure (Christopher et al., 2017). Moreover, RHA has a hydrophilic nature and absorbs the free water presented in the slurry. As such, once the percentage of RHA goes from 5 to 10%, superplasticizer might be needed to maintain the workability of the cement. It should be noted that all the RHA based cement passed the threshold of free water test which is 5.90% as per the API-10A.

5.3.3 Rheology

To determine the rheological parameters of the RHA based cement, API standard 10-B was used. Experimental readings were taken by atmospheric rotational viscometer (Fann model 35) at different RPM as described earlier. The preparation stages were similar to the procedures explained earlier for the POFA based cement. The results obtained from the rheological measurements are shown in and summarised in Table 5-6. To ensure the consistency of the result, each test was repeated twice. Figure 5-3 shows the result obtained from the cement with 5 wt% RHA which highlights the fact that the results are consistent, and the procedure followed is trustworthy.

Table 5-6: Plastic viscosity and yield point of RHA based cement

RHA Content (%)	Plastic Viscosity (cP)	Yield Point (lb/100ft^2)
0	145.74	34.563
1	144.4	34.08
2	153.26	35.25
3	172	32.16
4	185	33.63
5(a)	183.3	35.66
5(b)	182.6	32.76

From Table 5-6, it can be seen that the rheological properties of the neat cement and 1% RHA are very close. This is due to the fact that a small amount of cement was replaced by RHA. However, as the quantity of RHA in the cement increases, the plastic viscosity increases. The percentage increase of the plastic viscosity between the neat cement and 2, 3, 4 and 5wt% RHA is around 5.031, 16.53, 23.74 and 22.7% respectively. The increase of the plastic viscosity is linked to the large surface area of RHA which can absorb the mixing water (Van et al., 2013). This absorption reduces the quantity of free water and increases the rheological properties of the cement.

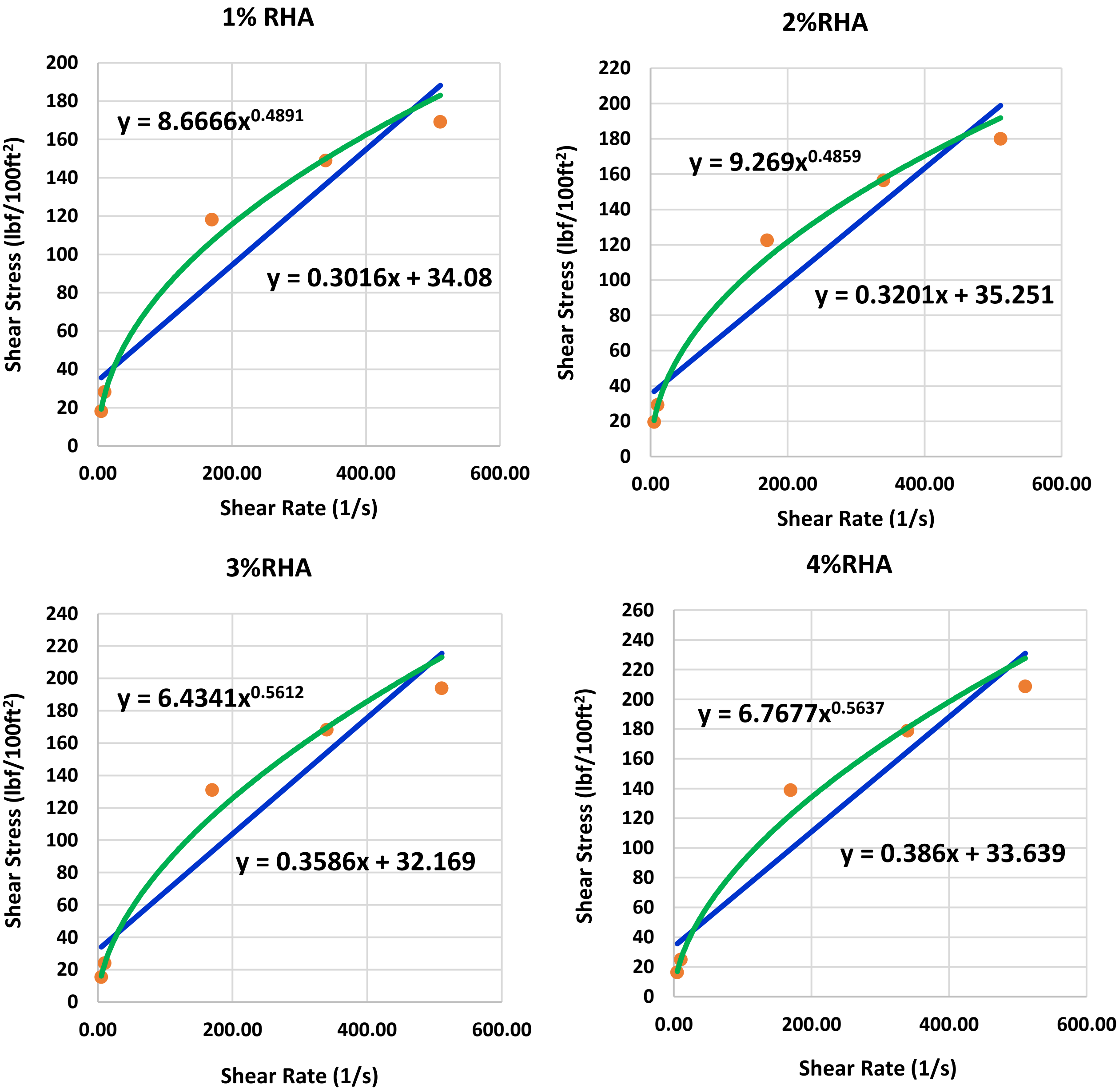


Figure 5-2: Rheology of the neat cement and RHA based cement composites

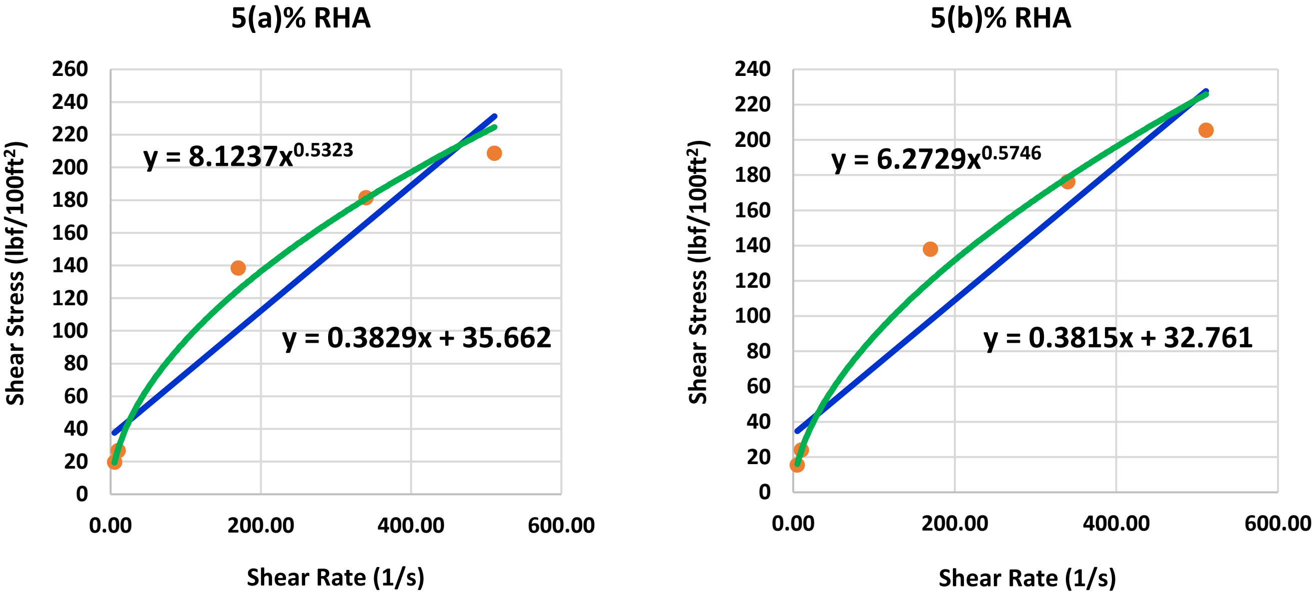


Figure 5-3: Comparison between the rheological behavior of two cement with 5 wt% RHA

5.3.4 Compressive Strength

5.3.4.1 Non-Destructive Test

As it was mentioned in the earlier chapters, compressive strength is an important property to evaluate the integrity of the cement. There are two ways to measure the strength which are called non-destructive and destructive methods. For the RHA based cement both methods were used to measure the strength in a real time. The non-destructive were done first using the UCA machine and the procedure used was the same as the one applied for POFA based cement. The test was done under the temperature of 50°C and pressure of 2200PSI for 24 hours. Figure 5-4, Figure 5-5 and Table 5-7 shows the result of the compressive strength obtained from the UCA.

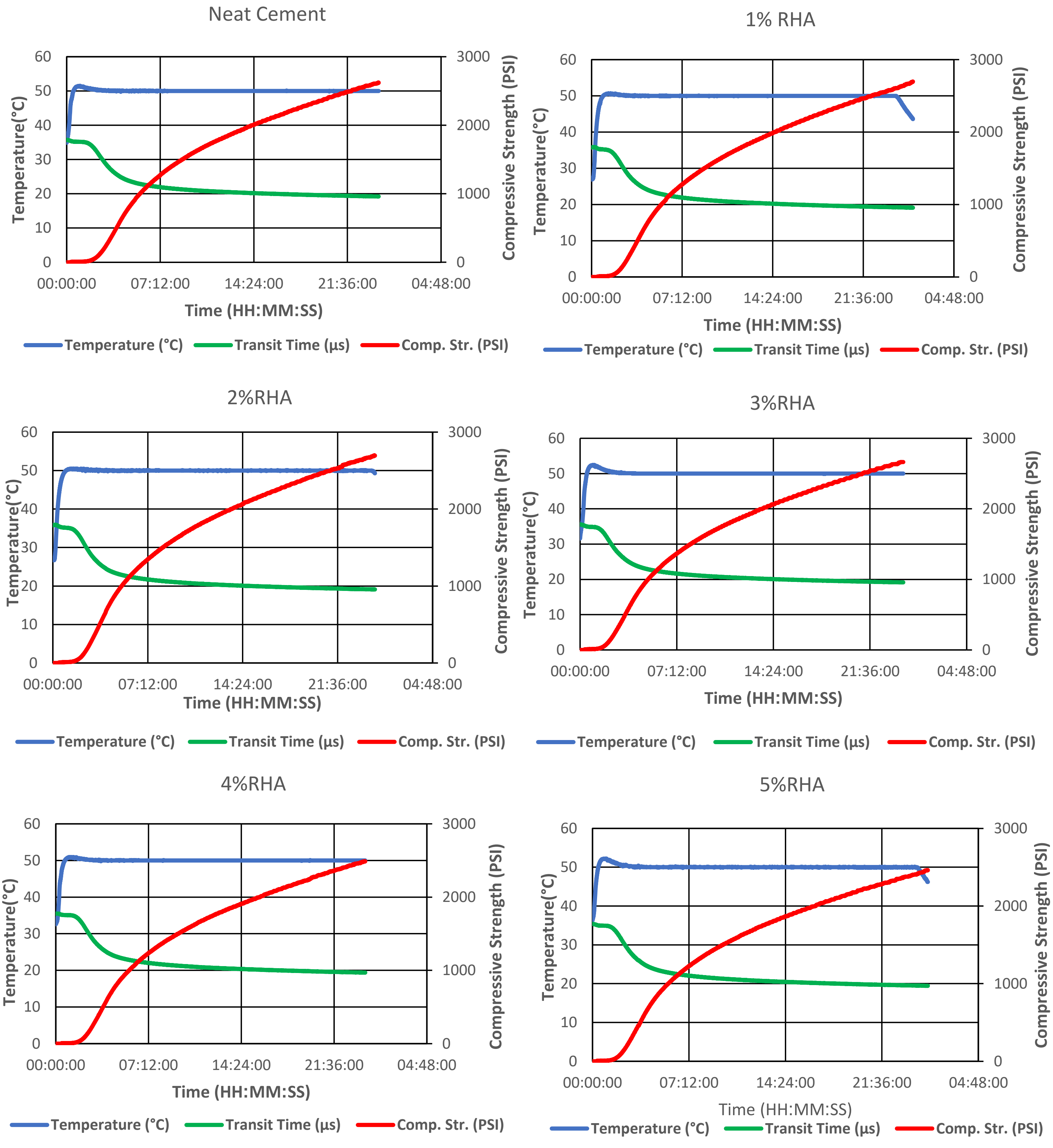


Figure 5-4: Real time strength of the RHA based cement obtained from the UCA

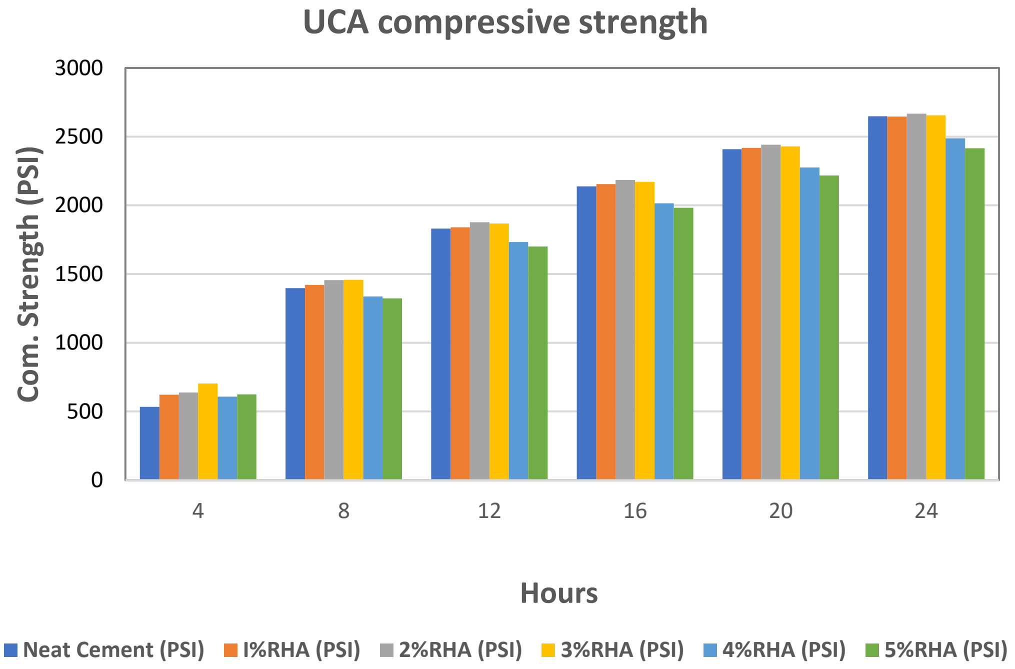


Figure 5-5: Bar chart of RHA cement composite obtained from UCA after 24 hours of test

Table 5-7: Compressive strength of different cement composites after 24 Hours of test in UCA

Time (Hours)	Neat Cement (PSI)	I%RHA (PSI)	2%RHA (PSI)	3%RHA (PSI)	4%RHA (PSI)	5%RHA (PSI)
4	533.4267	622.98	638.315	703.6	608.48	623.67
8	1397.4	1421.125	1456.12	1458.995	1337.62	1323.265
12	1831.433	1839.187	1876.425	1867.68	1733.72	1701.665
16	2137.62	2154.78	2183.87	2171.725	2014.07	1981.21
20	2409.383	2418.765	2440.39	2429.26	2275.57	2217.025
24	2647.873	2645.95	2666.56	2654.49	2487.43	2414.41

From Table 5-7, it can be seen that the compressive strength of 1 wt% RHA replacement is almost the same as that of the neat cement. A very similar trend in the rheology was observed when 1 wt% RHA was added to the cement. However, when the quantity of RHA increases, the compressive strength increases especially in the cement with 2 and 3 wt% RHA. On the other hand, 4 and 5 wt% RHA based cement showed a lower compressive strength than the neat cement. The decrease in the compressive strength could be due to the fact that RHA is not in a good quality and contains impurities that impaired its functionality. Moreover, replacing the cement with RHA will reduce the quantity of Portlandite and C-S-H. It was concluded that addition of RHA can be done up to 3 wt% without having any deleterious effects on the compressive strength of the cement.

The result of WOC (Table 5-8) also showed that all the cement prepared by adding RHA have a lower Wait on Cement (WOC) compared to the neat cement. The lowest time was recorded for 3 wt% RHA based cement which was about 30 min less than the neat cement. This result showed that at the early stage of curing, RHA acts as an accelerator but as time passes it may become a retarder and slows down the process of hydration.

Table 5-8: WOC for the RHA cement composite

RHA Content (%)	**WOC (HH:MM: SS)**
NC	03:54:11
RHA1%	03:37:52
RHA2%	03:36:26
RHA3%	03:24:22
RHA4%	03:40:12
RHA5%	03:36:37

5.3.4.2 Destructive Test

Destructive test for the measurement of the RHA based cement was carried out using the semi-automated triaxial testing machine. The sample used for the destructive test had cylindrical shape with a dimeter and length of 1 inch. The samples used for the destructive tests were cured in the water bath at the temperature of 50°C and atmospheric pressure for one day and was left in the ambient condition for rest of the 14 days. The loading rate of the machine was kept at 18kN/min. Table 5-9 gives the destructive compressive strength of different RHA based cement.

Table 5-9: Compressive strength of the RHA cement composite

RHA Content (%)	Compressive Strength (MPa)
0	41.57
1	44.50
2	39.08
3	40.07
4	34.95
5	38.56

From the result obtained, it was found that the highest compressive strength is achieved when 1 wt% RHA is replaced in the cement. On the other hand, all other samples had a lesser compressive strength than the neat cement. However, reduction in the compressive strength of 2 and 3 wt% was only 6.17 and 3.7 % less than the neat cement while that of 4 and 5% RHA was a bit higher reaching 17.3 and 7.5% respectively. Thus, it was concluded that above the replacement level of 3 wt% of RHA, the cement will be saturated, and the compressive strength starts to drop. This reduction in the compressive strength was observed in both destructive and non-destructive tests. Thus, cement can be replaced by RHA up until 3 wt% without having any deleterious effects on the compressive strength of the composite.

5.3.5 Thermogravimetric Analysis (TGA)

For the chemical characterization of the RHA cement composite Mettler Toledo Thermogravimetric Analysis (TGA) was used. The principle at which the TGA work depends on the weight loss of the sample when subjected to the heat. To analyse the pozzolanic activeness of the RHA, the dehydroxylation of the Portlandite was targeted. The purpose of characterizing the quantity of the Portlandite is the fact that during the pozzolanic reaction the silica present in the RHA reacts with the Portlandite in the cement composite and produces secondary C-S-H. Hence, reduction in the quantity of the Portlandite in the cement will be an indication of the pozzolanic reaction and increase in the compressive strength. The parameters of the TGA test were kept the same as those used for POFA based cement. The samples used for the TGA test were cured in the UCA condition for one day and were left out in the ambient condition for almost 3 months. The result obtained are shown in Figure 5-6 and Table 5-10.

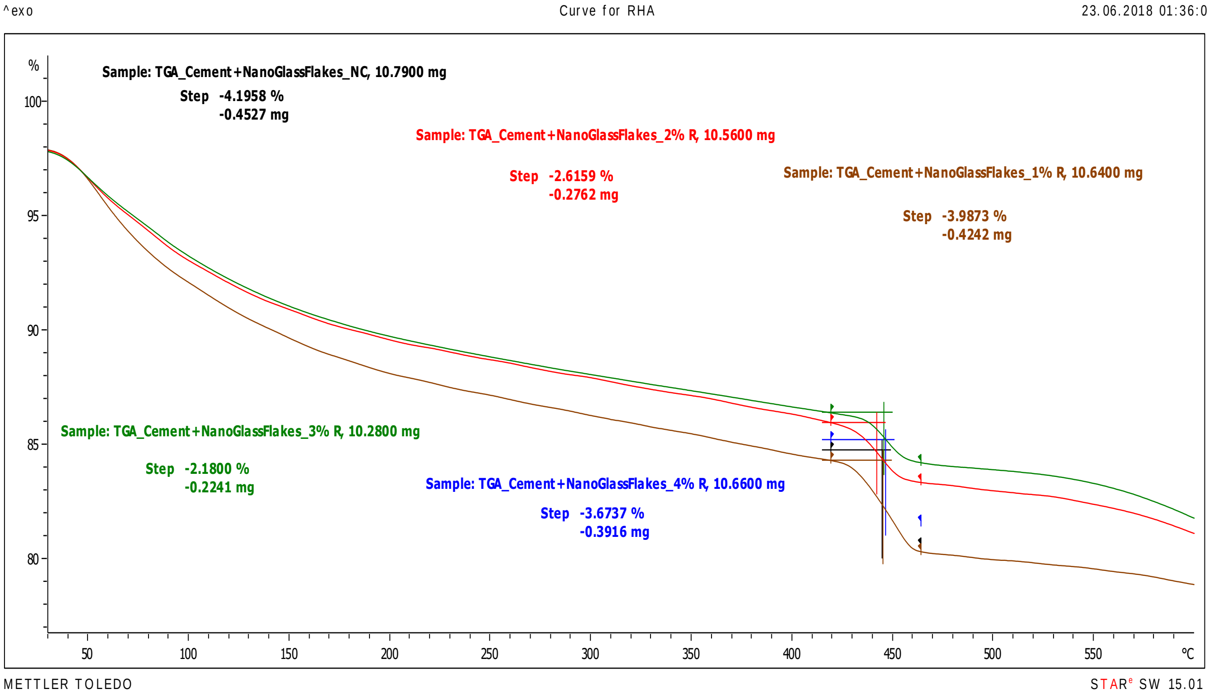


Figure 5-6: TGA curves of different RHA based cement samples

Table 5-10: Amount of Portlandite left in the RHA based cement after 3 months of curing

RHA Content (%)	Amount of Portlandite (%)
0	17.2737
1	16.41002
2	10.7755
3	9.04813
4	15.09393

As it is seen in Table 5-10, as the quantity of RHA in the cement increases, the amount of Portlandite decreases as long as the quantity of replacement does not exceed 3 wt%. Although this test should be interpreted separately from the compressive strength measurements because the TGA test was done after three months of curing, it was evident that the RHA replacement must be done up until 3 wt% to get a good compressive strength. The decrease in the amount of Portlandite is due to the pozzolanic reactions that transformed Portlandite into the secondary C-S-H. However, the reason why the cement with 4 wt% RHA has a higher amount of Portlandite can be linked to the fact that saturation has reached and RHA added to the cement is not contributing into any pozzolanic reactions. It should be noted that the TGA test for 5 wt% RHA was not carried out because the saturation was already reached and the compressive strength measured was low for 4 and 5% RHA based cement.

5.4 Discussion

The purpose of this chapter is to present a general over view of the reactions induced by RHA once added to the well cement. No comparison was made between RHA and POFA or Nano Silica since the samples had a different curing time. However, it was observed that addition of RHA will not have any significant effect on the density of Class G cement. The free fluid test showed that as the quantity of RHA in the cement increases, the amount of free fluid decreases because RHA has a highly porous nature because of its honey comb like structure that makes it a hydrophilic pozzolanic material. It was also found that RHA increases the workability of the cement due to the low availability of free water. All of the RHA based cement had a higher plastic viscosity than the neat cement except the one with 1 wt% RHA that showed a similar value as that of the neat cement. The results obtained from the non-destructive tests in the UCA indicated that samples with 2 and 3 wt% RHA have a higher strength than the neat cement. Looking the results obtained from the destructive tests performed on the samples cured for 14 days highlighted that the compressive strength of 1 wt% RHA is higher than the neat cement. However, any replacement above 3 wt% would decrease the compressive strength. The WOC of all cement samples revealed a lower time to reach 500PSI than the neat cement. This emphasised that RHA in the early stage act as an accelerator and as time passes would retard the development of the compressive strength in the cement.

5.5 Conclusions

The results obtained from this study indicated that RHA has the potential to enhance the properties of Class G cement due to its pozzolanic reactions. However, the replacement of RHA in the cement should not be more than 3 wt% as it would decrease the compressive strength of the cement composites. This is due to the fact that saturation of RHA in the cement is reached and any further replacement above 3 wt% of RHA in the cement will not contribute in enhancing the strength of the cement. It was also concluded that RHA will act as accelerator in the early stages of hydration and will retard the hydration rate as time passes.

Chapter 6: Carbonation of Cement Composites with Nano Particles and Agricultural Wastes

6.1 Introduction

From the literature it was seen that the chemical composition of the neat cement makes it susceptible to the carbonation when exposed to the acidic environment. In the CCS (Carbon Capture and Sequestration) environment the well cement will be attacked by the supercritical (sc) CO_2 that will compromise the durability of the cement. The attack of scCO_2 is much sever and faster than the CO_2 in any other form because scCO_2 has the properties that is in between the gas and liquid. To be specific scCO_2 have the density of the liquid CO_2 and diffusivity of gas. Moreover, when scCO_2 get dissolves in the water it creates carbonic acid whose pH is less than 6, while the pH of cement is more than 12.5. Due to the difference in the pH the ingression of the CO_2 in the cement matrix take place. The condition in which the scCO_2 exist is when the temperature and pressure is higher than 31.10°C and 1070PSI respectively.

The first component of the cement composition that is compromised by the attack of scCO_2 is Portlandite ($Ca(OH)_2$). The carbonation of the cement is a self-healing process that increase the compressive strength and decrease the permeability and porosity of the cement. In fact, there have been studies carried in which the high strength concrete is formulated by doing the carbonation on it. However, if the ingression of scCO_2 continues the carbonates in the cement due to carbonation will be converted to bicarbonate and will leach out of the cement and compromise the mechanical and transfer properties of the cement. After the Portlandite in the cement is consumed than the scCO_2 will start to attack the C-S-H which is the main binding material in the cement matrix and hence the durability of the cement will be compromised.

The focus of this study was to develop a cement composition by the addition of nano particles (NS) and agricultural waste (POFA and RHA) that can resist the attack of the scCO_2. However, samples that were subjected to the carbonation test should also have the best results in pre-carbonation test. From the previous chapters the composition that gave the best results were subjected to the water saturated scCO_2 for the time period of 40 days. After which the comparison was made between the samples. The test was also conducted on the samples in the pre-carbonation stage so that the comparison can be made with post carbonated samples. The test conducted for the pre-carbonation test consisted of compressive strength and measuring the mass of the samples. Whereas, for the post carbonation test phenolphthalein, compressive strength, microscopic image analysis, TGA and mass measurement was done. After the post and pre-carbonation test the composition that resisted the attack most was selected.

6.2 Methodology

6.2.1 Sample Preparation

The cement samples prepared and used for the carbonation test are shown in Figure 6-1 with their details given in Table 6-1. These samples were chosen given their good performance in the pre-carbonation test discussed in previous chapters. These samples were firstly cured in a water bath at the temperature of 50°C and atmospheric pressure for 24 hours and then exposed to the ambient condition for 28 days. This 28 days of curing was chosen since it could give enough time to have at least 70% of its hydration products generated (Costa et al., 2018). Moreover, this curing time could simulate the CCS scenario where CO_2 is injected in the well after the complete consolidation of the cement (Costa et al., 2018). It should be noted that the height to diameter ratio of the sample used for the carbonation was 1.

Table 6-1: Selected cement composite for the exposure of water saturate $scCO_2$

Sample No.	Content of RHA, POFA or NS (%)	Weight of RHA, POFA or NS(g)	Weight of Cement (g)	Mix water (g)
1	0	0	692	305
2	5 (POFA)	34.6	657.4	305
3	0.5 (NS)	3.46	688.54	305
4	0.75 (NS)	5.19	686.81	305
5	3 (RHA)	20.76	671.24	305

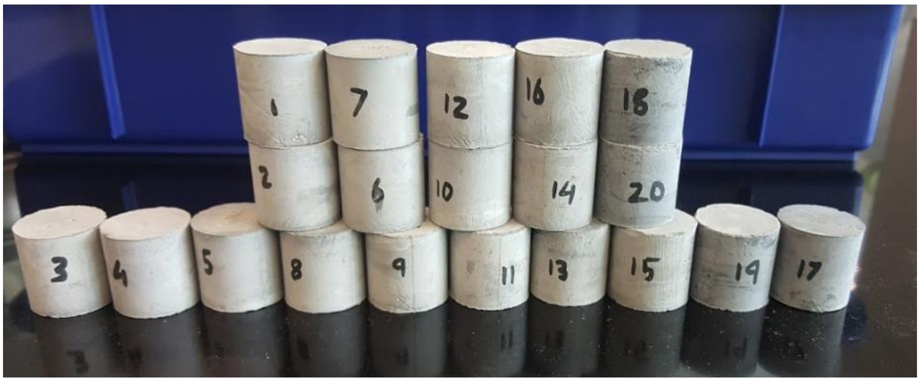


Figure 6-1 : Samples of different composition prepared for the carbonation test

6.2.2 Carbonation and Static Reactor Conditions

For the carbonation test of the samples, a special static reactor was designed for the purpose of this study whose schematic is shown in Figure 6-2. In this reactor, liquid CO_2 is used and injected in the cement sample holder as a super critical fluid by the help of the supercritical pump. Temperature can be increased by the thermocouple that is wrapped around the vessel of the static reactor. The pressure and temperature of the static reactor was kept above the critical point (i.e. 1070PSI and 31.10°C) for almost 40 days. The fresh water was placed in the vessel and changed 3 times during the course of the test in order to accelerate the interactions. However, it should be noted that water in the subsurface layers is brine but fresh water was used in this study to accelerate the carbonation rate since the solubility of CO_2 in fresh water is two times higher than the brine (Barlet-Gouedard et al., 2009). Verba and O’Connor (2010) also concluded that alteration rate is very high once samples are exposed to low saline water which might be due to high solubility of CO_2 in low saline water. Moreover, it was reported by Toews et al. (1995) that the dissolution of supercritical CO_2 in fresh water will reduce the pH to 3 and creates more severe interactions between the cement and CO_2 saturated water. It should be noted that water of the sample holder was changed 3 times during the test to remove the dissolve ion from the cement and increase the rate of carbonation in the samples. However, this condition is much severe than the condition in a real CO_2 storage site condition due to the presence of saline water which reduces the rate of reaction (Bachu et al., 1994). Thus, if the samples can survive such a harsh condition used in this study, they can certainly survive from the attack of CO_2 in a real storage site condition. Figure 6-4 shows the samples after being expose to the water saturated CO_2 for 40 days.

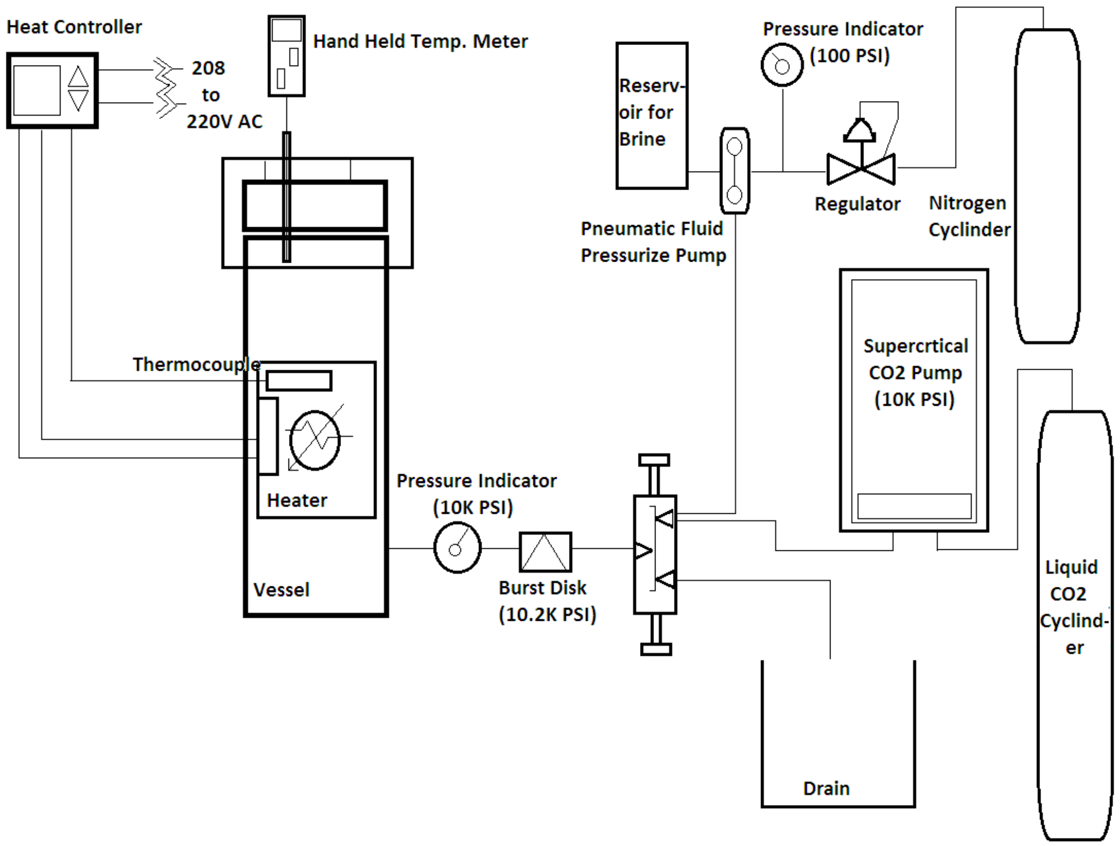


Figure 6-2: Static reactor schematic diagram

Figure 6-3: Static reactor used to expose the cement samples to water saturated $scCO_2$ for 40 days

Figure 6-4: Samples after exposure to water saturated $scCO_2$

6.3 Experiments and Discussion

6.3.1 Phenolphthalein Test

The phenolphthalein test was done to find out the carbonation depth of the samples after the carbonation test. To do this, the samples were slabbed in the longitudinal direction and phenolphthalein was applied on their fresh surfaces. Phenolphthalein is chemically expressed by $C_2OH_{14}O_4$ and known as a pH indicator. It changes the colour of the solution/solid and turns into purple or magenta once the pH goes above 10.5. It will remain colourless when the pH is less than 9 (Chinchón-Payá et al., 2016).

The solution of phenolphthalein was made by mixing 1g of phenolphthalein powder in 70ml of ethanol followed by adding 30ml of deionized water. The phenolphthalein solution was taken in the dropper and was placed on the carbonated samples. The penetration depth of the carbonation in the samples was then taken from the points where the deepest ingression of CO_2 was observed in the samples. The results obtained are shown in Figure 6-7 to Figure 6-11.

The results obtained indicated that the cement samples have gone through the carbonation after 40 days of the test (See Figure 6-5). It should be recalled that phenolphthalein must be dropped on the carbonated samples to provide representative results. Putting them on the samples that are not carbonated, will make the whole sample purple due to the presence of Portlandite which increases the pH of cement to 12.5. As it is seen in Figure 6-6, different samples have different carbonation penetrated depth. Carbonation of the samples was measured from the outer boundary of the sample to the boundary of the coloured region in the centre. For the comparison purposes, the neat cement was taken as the reference. It was then found that the neat cement was attacked from three different sides (right, left and bottom) and the maximum carbonation depth was 0.9cm from the left side. The carbonation depth in the right and the bottom side was around 0.6cm.

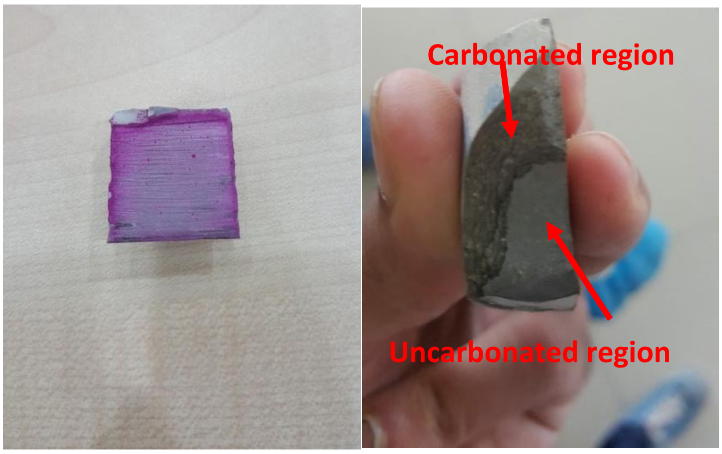


Figure 6-5: Left) Uncarbonated sample with phenolphthalein test and right) carbonated sample without the phenolphthalein test

It was also highlighted that the cement sample consisting mainly of the agricultural waste did not perform well in the test and had a larger carbonation depth then the neat cement. Nano Silica based cement samples, on the other hand, showed a better resistance against the attack of water saturated $scCO_2$ than the neat cement. The maximum depth of carbonation for the sample with 3 wt% RHA was around 0.85cm while that of 5 wt% POFA based cement was around 0.9cm. It was then found that the cement sample with 0.5 wt% Nano Silica has the best performance as the carbonation depth was only around 0.4cm from the both left and right sides. The sample with 0.75 wt% Nano Silica also showed an outstanding behaviour with the carbonation depth of 0.5cm from the both sides. To have a better comparison and get a final conclusion on the performance of different samples, an image analyser software called Digimizer was used to measure the area of the carbonated and uncarbonated zones in the samples. The results obtained from the image analysis are shown in Figure 6-12 and reported in Table 6-2 and Figure 6-13.

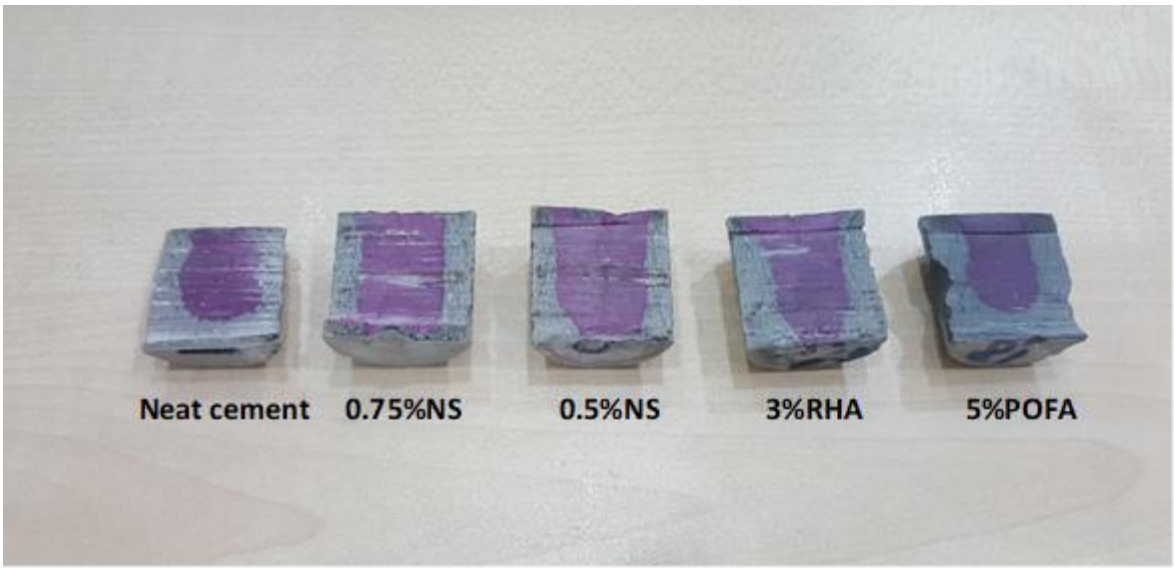


Figure 6-6: Phenolphthalein test on the carbonated samples of different cement composite

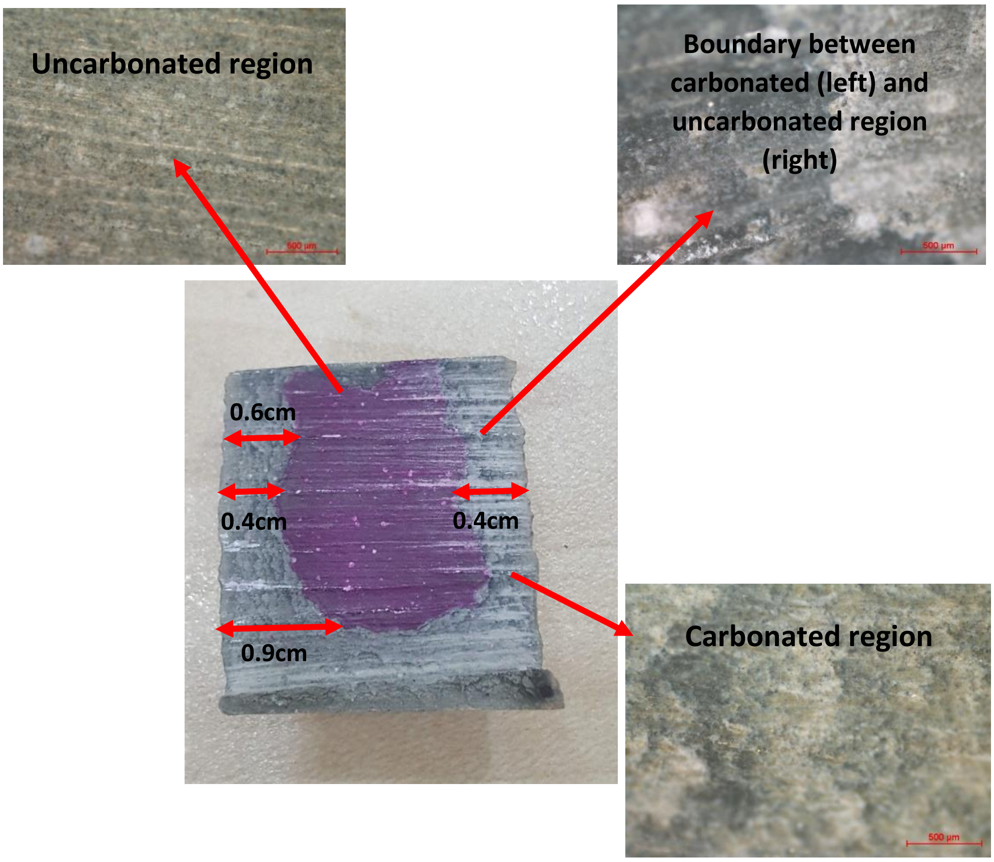


Figure 6-7: Carbonation of neat cement after 40 days of exposure to water saturated $scCO_2$

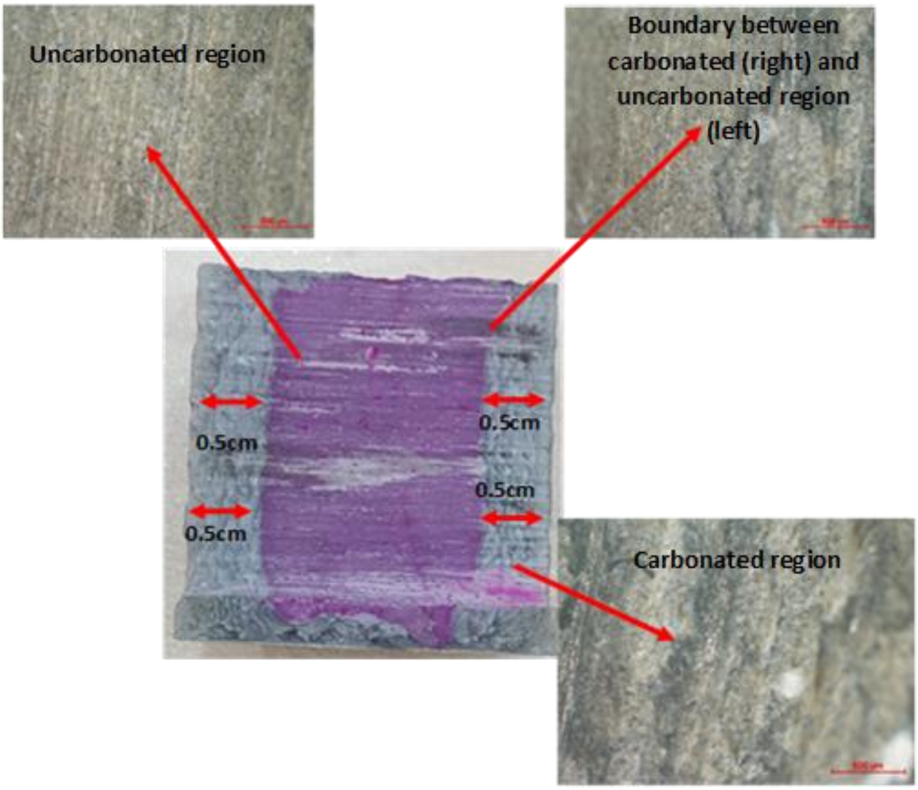


Figure 6-8: Carbonation of 0.75 wt% NS after 40 days of exposure to water saturated $scCO_2$

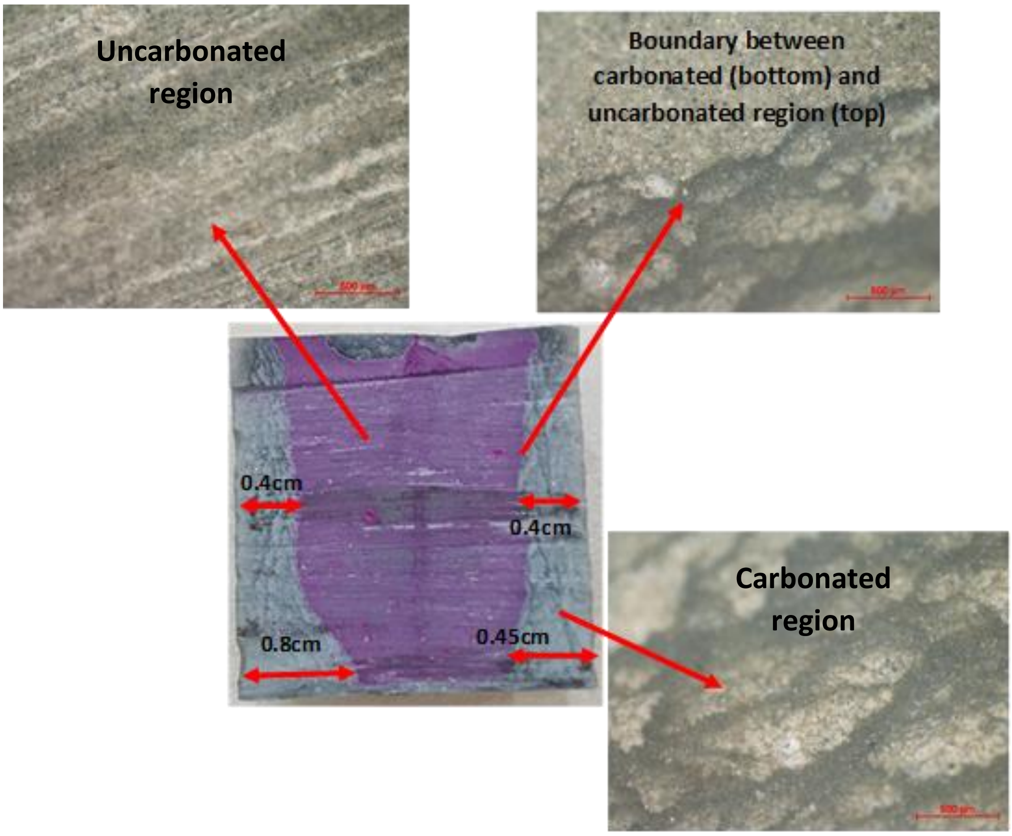


Figure 6-9: Carbonation of 0.5 wt% NS after 40 days of exposure to water saturated $scCO_2$

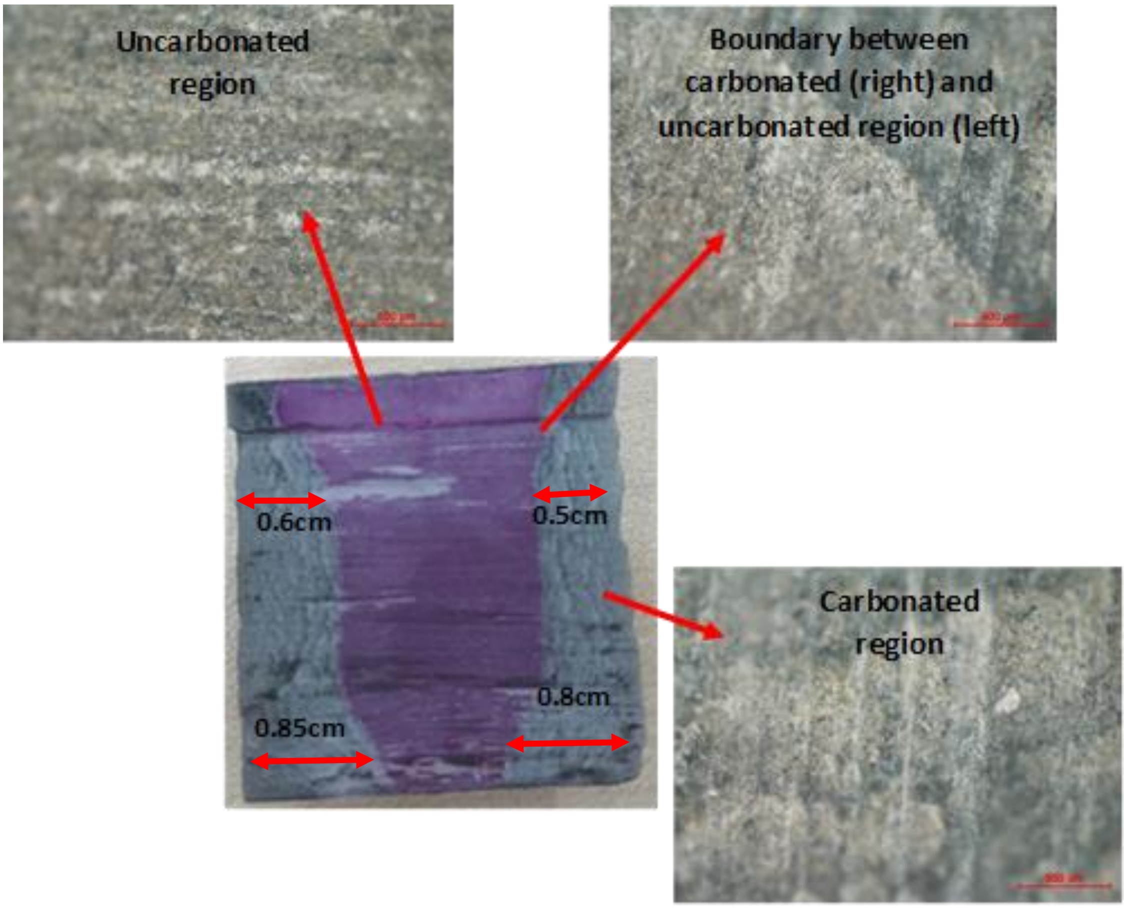


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Figure 6-10: Carbonation of 3 wt% RHA after 40 days of exposure to water saturated $scCO_2$

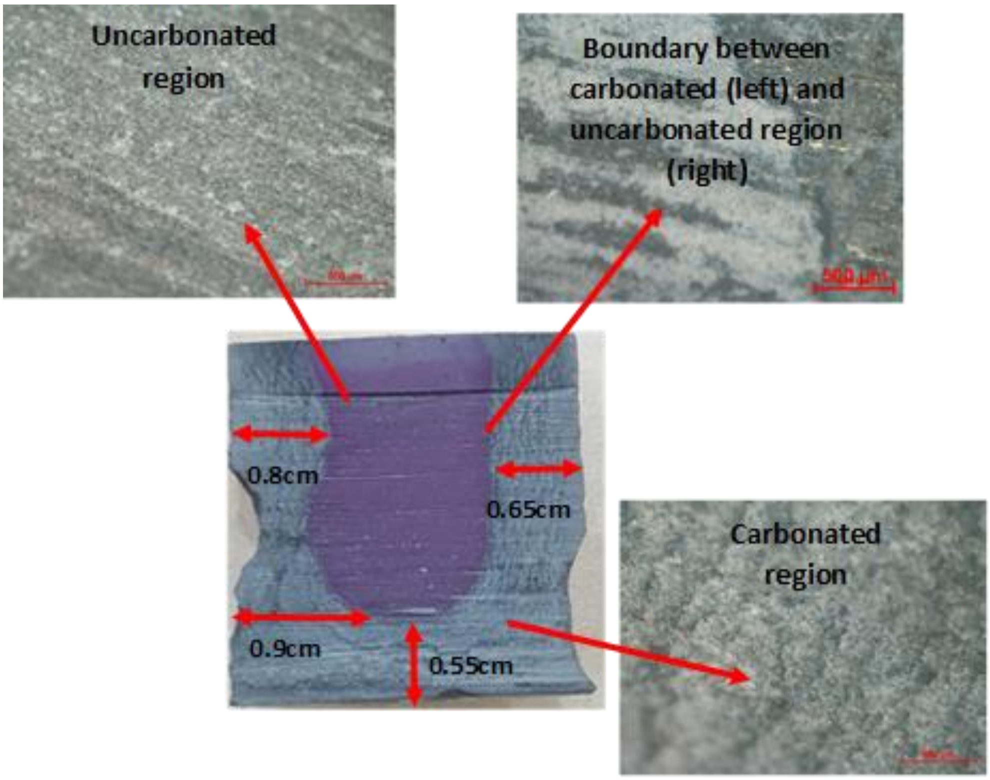

Figure 6-11: Carbonation of 5 wt% POFA after 40 days of exposure to water saturated $scCO_2$

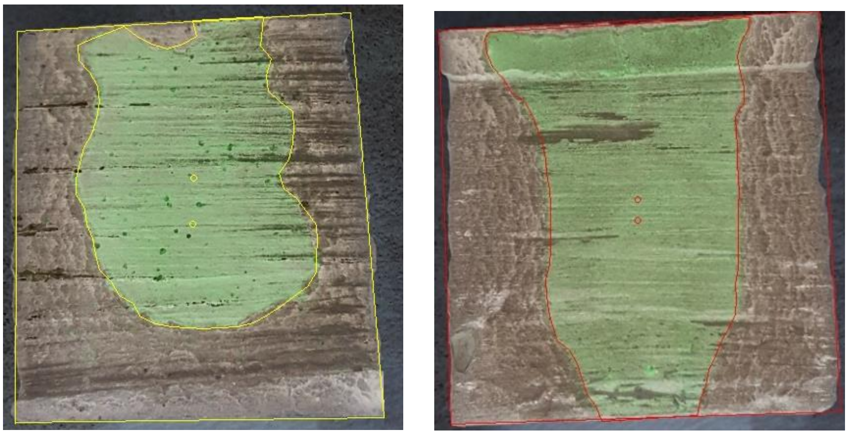

Figure 6-12: Measurement of the carbonated area with the image analyzer software. Neat Cement (left) and 3 wt% RHA (right)

Table 6-2: Percentage of carbonated and uncarbonated areas in different cement samples

Cement composite	**Uncarbonated area (%)**	**Carbonated area (%)**
Neat Cement	41.05	58.95
0.75%NS	56.1	43.9
0.5%NS	59.28	40.72
3%RHA	48.4	51.6
5%POFA	36	64

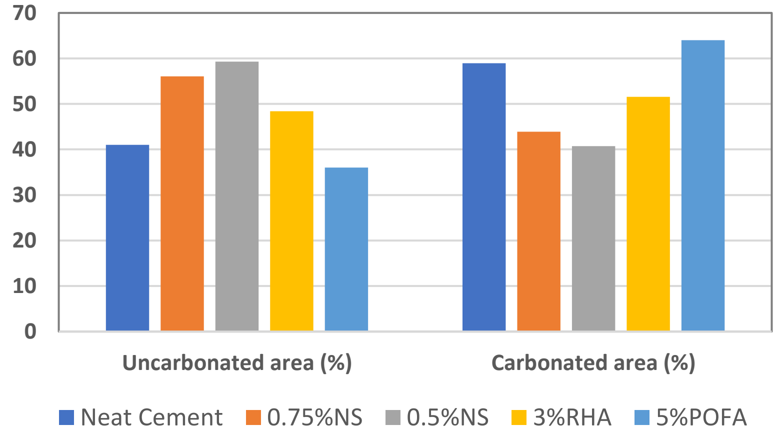

Figure 6-13: Bar chart representing the carbonated and uncarbonated area of different cement composites

From the Figure 6-13, it appears that Nano Silica based cement samples have a better performance than the agricultural waste-based cement. This could be linked to the particle size and purity of Nano Silica. It should be noted that agricultural wastes had particles in the micro size and contained impurities as reported earlier in the XRF results. However, promising result were shown as all the cement composite performed better than the neat cement except for the 5wt% POFA. The reason could be the fact that POFA act as the retarder in the cement and takes time to improve the properties of the cement. Therefore, 28 days of curing would not be sufficient to generate the consolidate cement matrix that can resist the attack of $scCO_2$. Whereas, for the NS cement composite, the presence of nano scale silica particle will accelerate the pozzolanic reaction of the cement and will create a dense and consolidated cement matrix that can resist the attack of $scCO_2$. Moreover, the POFA particle shape is irregular in nature and increases the transfer properties. Whereas, for the NS the shape is regular and will act as the filler in the cement matrix that decreases the transfer properties of the cement. From the microscopic images rough surfaces of cement is evident in the carbonated area that shows that the cement matrix has been weakened. Whereas, for the uncarbonated section smooth surfaces can be seen.

6.3.2 Compressive Strength

To further evaluate the degree of carbonation that the cement samples are gone through, a series of destructive test was performed on the samples before and after the exposure to $scCO_2$. The procedure of performing the test was similar to what was explained in the previous chapters. The results obtained are summarised in Table 6-3 and shown in Figure 6-14.

The results obtained indicated that the compressive strength of the agricultural waste-based cement reduces after the carbonation while that of the neat cement and the Nano Silica based cement it increases. It also appeared that the sample with 0.75 wt% Nano Silica has the highest compressive strength before and after the carbonation.

Table 6-3: Compressive strength of the cement samples before and after the carbonation

Cement composite	**Before Carbonation (MPa)**	**After Carbonation (MPa)**	**Percentage of changes in compressive strength**
Neat Cement	36.43	68.71	68.71
0.75%NS	40.99	72.11	55.03
0.5%NS	35.35	67.03	61.9
3%RHA	32.57	26.73	-19.7
5%POFA	35.25	26.83	-27

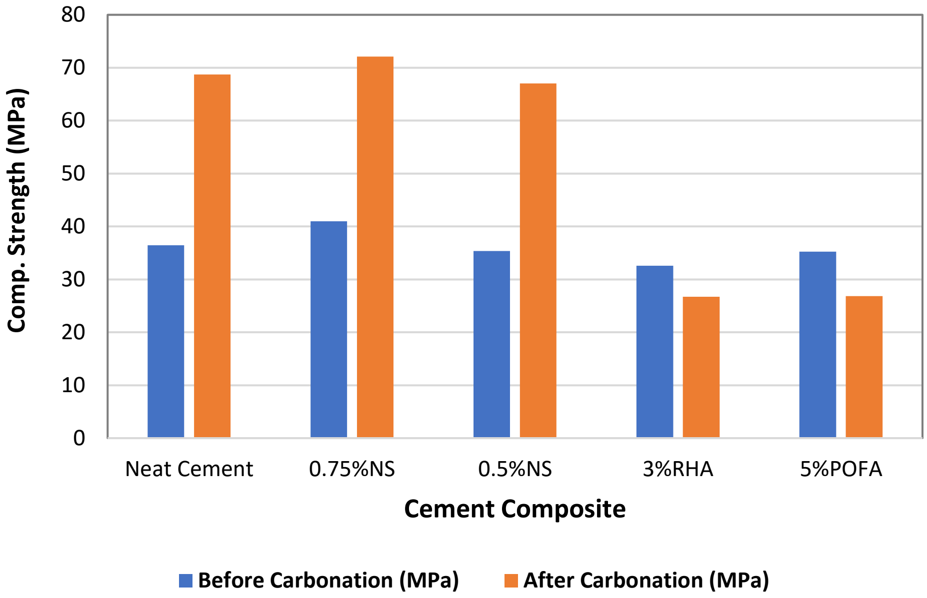

Figure 6-14: Compressive strength of the cement samples before and after the carbonation

This increase in the compressive strength could be due to the carbonation of Portlandite which produces calcium carbonates ($CaCO_3$). This calcium carbonate can precipitate in the pore structure of the cement with a molar volume 36.9 cm^3 causing reduction in the transfer properties and increase in the compressive strength. However, if the ingression of CO_2 continues, this carbonate is transformed into to calcium bicarbonate and is leached out of the cement matrix, resulting in significant loss of cement durability. Having said that, the reason behind the reduction of the compressive strength in the agricultural waste based cement can be the bi-carbonation process which was initiated soon due to the rapid consumption of Portlandite. These results were aligned with the phenolphthalein test that showed highest carbonated area was from the 5wt% POFA and the lowest compressive strength was also from the same sample. Whereas, Nano Silica cement composite showed highest compressive strength and lowest carbonated area.

6.3.3 TGA Tests

TGA was also carried on the carbonated samples to quantify the amount of Portlandite left in the sample after being exposed to $scCO_2$. The set up used for the TGA was the same set up applied and explained earlier in the previous chapters. The temperature, however, was varied from 20 to 1000°C for a better result. In the first part of the analysis, the amount of Portlandite left in the sample was measured while in the second part the weight loss in the samples was recorded after the dehydroxylation of calcium hydroxide. The purpose of quantifying the amount of Portlandite is that the attack of $scCO_2$ will reduce the quantity of the Portlandite and will convert it into calcium carbonate and hence the amount of Portlandite will be reduced. The equation used for the calculation of the Portlandite was the similar to the one used in the previous chapters. The results obtained from this stage are reported in Table 6-4 and shown in Figure 6-15.

It can be seen from the TGA analysis that the Nano Silica based cement have a higher amount of Portlandite in their structure whereas the amount of Portlandite left in the POFA and RHA based cement is lesser then the neat cement. It appears that the largest amount of Portlandite left in the sample belongs to the sample with 0.5 wt% Nano Silica while the smallest amount of Portlandite was found in the 5 wt% POFA based cement. As it was mentioned earlier, the quantity of Portlandite left in the samples indicate the level of carbonation and bi-carbonation that each cement sample has gone through in the carbonation test. Whereas, from the temperature range of 530 to 950°C the mass loss of CO_2 from the carbonation take place and it was recorded that within that temperature range the highest amount of mass loss was from the 5 wt% POFA that was 23.6% and the lowest was from the 0.5 wt% NS cement composite that was 16.5%.

Table 6-4: Quantity of Portlandite left in different cement samples after carbonation

Cement composition	Weight loss (%)	Amount of Portlandite (%)
Neat cement	1.29	5.30
0.75% NS	0.96	5.08
0.5%NS	1.31	6.64
3% RHA	0.66	4.37
5% POFA	0.69	3.0

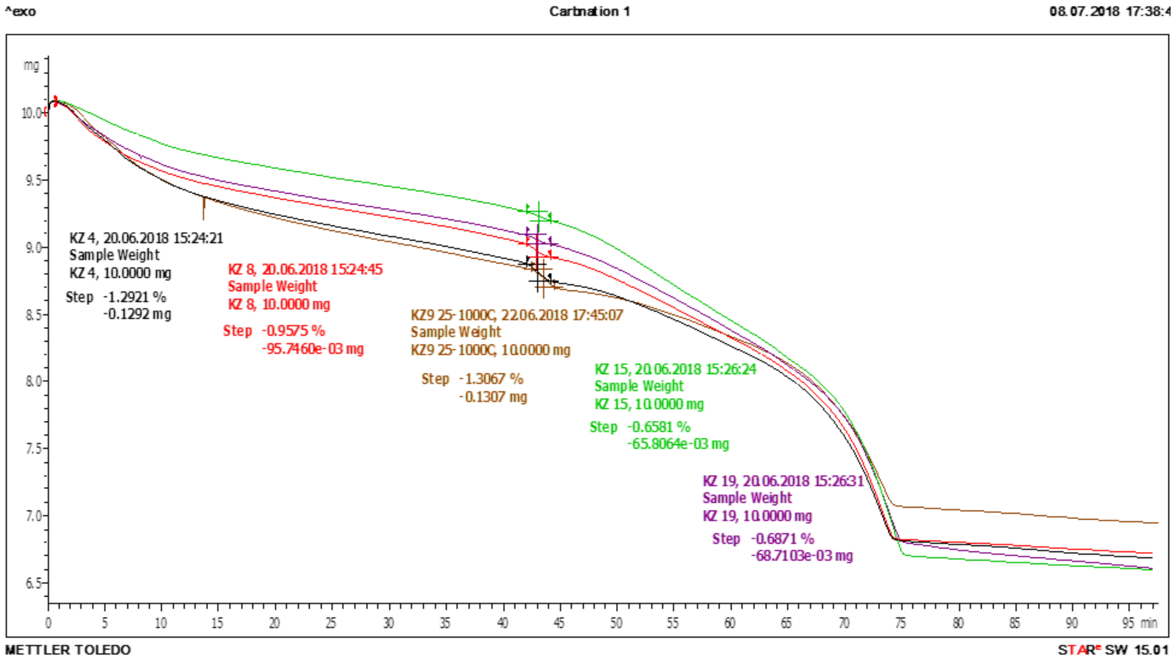

Figure 6-15: TGA of cement samples after the carbonation test

6.3.4 Mass Measurements

Measurements of the mass was also done as part of the post carbonation test. It should be noted that due to carbonation and bi-carbonation, the mass of the samples may increase or decrease respectively. This is due to the high molar mass of $CaCO_3$ (100.0869 g/mol) in the carbonation that replaces Portlandite having the molar mass of 74.093 g/mol. Hence, after the carbonation process in which Portlandite is converted into $CaCO_3$, the mas of the samples increases while transformation from $CaCO_3$ to $Ca(HCO_3)_2$ decreases the mass. The results obtained from the mass measurements are shown in Figure 6-16. As it is seen in the figure, the mass of all cement samples has increased which indicates the fact that carbonation was initiated but bi-carbonation has not been deeply taken place yet. It was also found that the least percentage increase belongs to the sample with 0.5 wt% Nano Silica and the sample with 3 wt% RHA has the highest mass gain. Interestingly, the mass gain of 5 wt% POFA based cement was less than the sample with 3 wt% RHA but was more than any other cement composites. This is due to the fact that the bi-carbonation process has already started in the sample with 5 wt% POFA, leaching calcium carbonate out of the cement matrix.

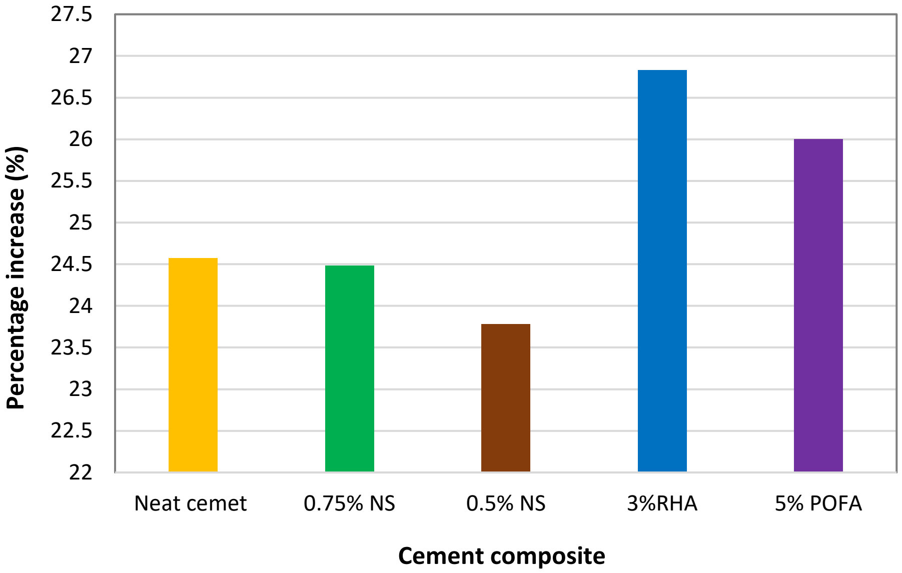

Figure 6-16: Percentage increase in the sample mass of different cement composition after carbonation

6.4 Conclusions

From the experimental studies performed on the cement samples after the carbonation test for 40 days, it was found that the carbonation has taken place in all cement composites. However, the samples with Nano Silica performed far better than the cement with the agricultural wastes. This could be linked to the particle size and purity of Nano Silica that makes it an excellent pozzolanic material. Moreover, Nano Silica has a large surface area that increases the pozzolanic activity and produces more secondary C-S-H that will reduce the transfer properties of the cement. On the other hand, the agricultural wastes used in this study had impurities that could impair the properties of the cement composite once added. Moreover, the shape and the size of the agricultural waste further compromise the performance of the agricultural waste composite in the $scCO_2$ environment. It was concluded that the sample with 0.5 wt% Nano Silica has the best performance against carbonation while the sample with 5wt% POFA is the worst sample for the CO_2 storage site. Hence, Nano Silica based cement samples are recommended for the cement operational practice used to seal off the wells in the CO_2 storage sites.

Chapter 7: Conclusions and Recommendations

7.1 Conclusion

Carbonation of the neat cement takes place due to the reaction with dry/wet $scCO_2$ in a storage site which is a self-healing process and reduces the porosity and increases the compressive strength of the cement. However, due to the continuous diffusion of HCO^{3-}, bi-carbonation of $CaCO_3$ causes cement degradation. This degradation is characterized by increasing the porosity and permeability of the cement and reduction of the mechanical strength. According to the laboratory studies, parameters controlling the rate of carbonation in Portland cement can be divided into two categories of controllable and uncontrollable factors as reported in Table 7-1.

Table 7-1: Controllable and uncontrollable factors in the carbonation process of the cement

Controllable	Uncontrollable
Water to cement ratio	Temperature
Use of pozzolanic material	Partial pressure of CO_2
Decrease in porosity	Salinity of the formation water
Decrease in permeability	Static or dynamic condition
Provide tortious for CO_2 diffusion	Water to rock ratio

Pozzolanic materials may have a positive or negative impact on the cement resistance. Needle to say, these materials can enhance the resistance against the attack of CO_2 since they decrease or totally eliminates Portlandite. However, a large quantity of pozzolanic materials may have a negative impact on the rheology, free fluid and strength of the cement. The result obtained from the field also suggested that the pozzolanic cement could maintain its durability even after 30 years of exposure to a CO_2 rich environment. Thus, this study recommends the use of agricultural waste and nano materials including Palm Oil Fuel Ash (POFA), Rice Husk Ash (RHA) and Nano Silica (NS) which can improve the overall performance of the cement by the pozzolanic reactions. They have also been successfully tested against the corrosive environment in civil industry.

In the first part of the study, it was attempted to achieve a proper dispersion method for Nano Silica such that the cement can provide a consistent rheology and good compressive strength. It was found that the mixing approaches presented in the literature is unable to give a consistent rheological result. Hence, a new mixing technique was developed by the sonication method that was able to give a consistent result in rheology. Moreover, the new mixing technique was able to give a high compressive strength, low WOC and more dense cement matrix than the literature mixing approach. However, if the dispersion parameters are changed, the quantity of NS needed for a better performance of the cement would change.

In the studies carried on the POFA based cement samples, it was found that POFA can replace the cement by as much as 15% without having any deleterious effect on the cement properties. However, the least amount of Portlandite and more densified surface was observed in the cement with 5 wt% POFA. The rheological trend of the POFA cement composite was opposite to the trend that was observed by the NS based cement. This could be due to the fact that POFA may act like a filler and reduces the interlayer friction between the layers. It was also observed that POFA has a hydrophilic nature and retard the development of the compressive strength in the cement. The density of POFA based cement remained the same as that of the neat cement, although a slight drop in the density was observed when the replaced level of POFA goes above 15 wt%. It appeared that POFA can be a good choice for the development of the compressive strength without changing the rheology of the cement but its replacement level should not exceed certain limits.

A general study was also carried out on the RHA based cement to analyse the effect of an agricultural waste which contain more than 90% silica on the cement performance. It was found that like POFA, RHA has a hydrophilic nature. It was also observed that as the quantity of RHA increases, the free water in the cement slurry decreases and the plastic viscosity increases. It appeared that RHA acts as an accelerator in the early stages of hydration but turns into a retarder at the later stages. It also has its threshold limit of replacement and can replace the cement by as much as 3 wt%.

In the last part of the study, sample with the best performance were exposed to water saturated scCO_2 for 40 days. It was then found that the Nano Silica based cement can provide a better performance than the agricultural waste in a CO_2 storage site. This could be linked to the particle size of the Nano Silica and its large surface area. Moreover, the Nano Silica act as the accelerator in the development of the compressive strength while the agricultural wastes give a retarding effect to the cement. Impurities involved in the composition of the agricultural waste could be another reason behind their poor performance. It was, however, concluded that although the agricultural wastes may not provide a good resistance in the acidic environment, they can be used when cement with a high strength are required for maintaining the well integrity.

7.2 Recommendations

Given the low performance of the agricultural waste-based cement when exposed to water saturated $scCO_2$, it is recommended to improve the quality of the agricultural waste by burning them at a high temperature and reduce their particle size in order to make them more active. Furthermore, the agricultural wastes should be cured at different time interval to understand the curing period that gives a proper consolidation to the cement matrix.

For a better simulation of the reservoir condition, saline water should be used instead of fresh water and the test period should be increased to at least 3 to 6 months. The water in the static reactor should not be removed periodically as the flow rate in the subsurface layer are few millimetres to centimetre per year.

It is recommended to evaluate the effect of dispersant, retarder, fluid loss agent, anti-former, accelerator and extender on the overall performance of the cement used in this study. This could help to enhance the performance of the cement especially those agricultural wastes where unfavourable results were observed due to the natural characteristics of wastes.

References

Abdullah, K., M.W. Hussin, F. Zakaria, R. Muhamad, and Z. Abdul Hamid. 2006. "POFA : A Potential Partial Cement Replacement." *Proceedings of the 6th Asia-Pacific Structural Engineering and Construction Conference.*

Abid, Khizar, Raoof Gholami, Elochukwu Henry, Masood Mostofi, Chua Han Bing, and Golam Muktadir. 2017. “A methodology to improve Nano Silica based cement used in CO2 sequestration sites.” *Petroleum.*

Adam, Neil, and Tommie Charrier. 1985. *Drilling Engineeering a Complete Well Planning Approach.* Penn Well Pub. Co.

Ahmad, I. A., H. Parung, M.W. Tjaronge, and R. Djamaluddin. 2014. "Durability of Concrete Using Rice Husk Ash as Cement Substitution Exposed To Acid Rain." *Journal of Engineering Research and Applications* (Journal of Engineering Research and Applications) 4 (5): 144-149.

Ahmad, M. H. , R. C. Omar, M. A. Malek, N. Md Noor, and S. Thiruselvam. 2008. “Compressive Strength of Palm Oil Fuel Ash Concrete.” *ICCBT.*

Ahmed, Adil Elhag, and Farook Adam. 2007. "Indium incorporated silica from rice husk and its catalytic activity." *Microporous and Mesoporous Materials* 103 (1-3): 284-295.

Aiex, Cristina , Gilson Campos , Abhimanyu Deshpande, Abhinandan Chiney, Sandip Patil, and Kris Ravi. 2015. "An Experimental Study on Effects of Static CO2 on Cement under High-Pressure/High-Temperature Conditions." *SPE.*

Antiohos, S.K., V.G. Papadakis, and S. Tsimas. 2014. "Rice husk ash (RHA) effectiveness in cement and concrete as a function of reactive silica and fineness." *Cement and Concrete Research* 61-62: 20-27.

API. 2013. *Recommended Practice for Testing Well Cement: API Recommended Practice 10-B.* Amercian Petroleum Institue.

API. 2005. *Specification for cement and materials for well cementing: API specification 10A .* API.

Bachu, Stefan , Didier Bonijoly, John Bradshaw, Robert Burruss, Sam Holloway, Niels Peter Christensen, and Odd Magne Mathiassen. 2007. "CO2 storage capacity estimation: Methodology and gaps." *International Journal of Greenhouse Gas Control* 1 (4): 430-443.

Bachu, Stefan, and D. Brant Bennion. 2009. "Experimental assessment of brine and/or CO2 leakage through well cement at reservoir conditions." *International Journal of Greenhouse Gas Control* 3 (4): 494-501.

Bachu, Stefan, W.D. Gunter, and E.H. Perkins. 1994. "Aquifer disposal of CO2: hydrodynamic." *Energy Conservation and Management* 269-279.

Bai, Mingxing, Jianpeng Sun, Kaoping Song, Lili Li, and Zhi Qiao. 2015. "Well completion and integrity evaluation for CO2 injection wells." *Renewable and Sustainable Energy Reviews* 45: 556-564.

Bamaga, S. O., M. W. Hussin, and Mohamed A. Ismail. 2013. "Palm Oil Fuel Ash: Promising Supplementary Cementing Materials." *KSCE Journal of Civil Engineering* (KSCE Journal of Civil Engineering) 1708-1713.

Barlet-Gouédard, V. , G. Rimmelé, B. Goffé, and O. Porcherie. 2007. "Well Technologies for CO2 Geological Storage:." *Oil & Gas Science and Technology* 325-334.

Barlet-Gouédard, V., G. Rimmelé, O. Porcherie, N. Quisel, and J. Desroches. 2009. "A solution against well cement degradation under CO2 geological storage environment." *International Journal of Greenhouse Gas Control* 3 (2): 206-216.

Barlet-Gouedard, Véronique , Chatenay Malabry, Simon James, Bruno Drochon, Bernard Piot, and Caritey Jean-Philippe. 2012. Cement composition for carbon dioxide supercritical environment . Patent US 8,091,642 B2 . January 10.

Barlet-Gouedard, Veronique , Gaetan Rimmele, Bruno Goffe, and Olivier Porcherie. 2006. "Mitigation strategies for the risk of CO2 migration through wellbores." *SPE.*

Benge, Glen . 2009. "Improving wellbore seal integrity in CO2 injection wells." *Energy Procedia* 3523-3529.

Brandl, Andreas , Jennifer Cutler, Amanda Seholm, Michelle Sansi, and Gerald Braun. 2011. "Cementing Solutions for Corrosive Well Environments." *SPE.*

Carey, J. William. 2013. "Geochemistry of Wellbore Integrity in CO2 Sequestration: Portland Cement-Steel-Brine-CO2 Interactions." *Geoscienceworld.*

Chinchón-Payá, Servando , Carmen Andrade, and Servando Chinchón. 2016. “Indicator of carbonation front in concrete as substitute to phenolphthalein.” *Cement and Concrete Research* 87-91.

Chindaprasirt, P.,, and S. Rukzon. 2009. “Pore structure changes of blended cement pastes containing fly ash, riche husk ash and palm oil fuel ash caused by carbonation.” *Journal of materials in civil engineering* 666-671

Choolaeia, Mohammadmehdi, Ali Morad Rashidib, Mehdi Ardjmand, Amir Yadegari, and Hamid Soltanian. 2012. "The effect of Nano Silica on the physical properties of oil well cement." (Materials Science and Engineering A) 288-294.

Christopher, Fapohunda , Akinbile Bolatito, and Shittu Ahmed. 2017. "Structure and properties of mortar and concrete with rice husk ash as partial replacement of ordinary Portland cement – A review." *International Journal of Sustainable Built Environment.*

Costa, Sena, Bruno Leonardo de , Julio Cezar de Oliveira Freitas, Paulo Henrique Silva Santos, Dulce Maria de Araújo Melo, and Yvis Henrique de Oliveira. 2017. “Effects of carbon dioxide in Portland cement: A relation between static sedimentation and carbonation” *Construction and Building Materials* 450-458.

Costa, Sena, Bruno Leonardo de , Julio Cezar de Oliveira Freitas, Paulo Henrique Silva Santos, Dulce Maria de Araújo Melo, Romero Gomes da Silva Araujo, and Yvis Henrique de Oliveira. 2018. “Carbonation in oil well Portland cement: Influence of hydration time prior to contact with CO2.” *Construction and Building Materials* 252-260.

Deepak , T.J., Elsayed Albarra , Hassan Noor, N Chakravarthy, Yun Tong Siow , and B.M. Mithun . 2014. “Investigation on Properties of Concrete with Palm Oil Fuel Ash as Cement Replacement.” *INTERNATIONAL JOURNAL OF SCIENTIFIC & TECHNOLOGY RESEARCH* 3 (1).

Duguid, A., and G. Scherer. 2010. "Degradation of oilwell cement due to exposure to carbonated brine." *International Journal of Greenhouse Gas Control* 546-560.

Duguid, A., M. Radnojic, and G. Scherer. 2005. "Degradation of well cement exposed to carbonated brine." *Proceedings of the 4th Annual Conference on Carbon Capture and Sequestration.*

Duguid, Andrew , Mileva Radonjic, Robert Bruant, Thomas Mandecki, George Scherer, and Mike Celia. 2004. "THE EFFECT OF CO2 SEQUESTRATION ON OIL WELL CEMENT." *Proceeding of the 7th annual conference on greenhouse gas control technologies.*

Elyamany, Hafez E., Abd Elmoaty M. Abd Elmoaty, and Basma Mohamed. 2014. “Effect of filler types on physical, mechanical and microstructure of self compacting concrete and Flow-able concrete.” *Alexandria Engineering Journal* (Alexandria Engineering Journal) 53: 295–307.

Ershadi, V., T. Ebadi, A.R Rabani, L. Ershadi, and H. Soltanian. 2011. "The Effect of Nano Silica on Cement Matrix Permeability in Oil Well to Decrease the Pollution of Receptive Environment." (International Journal of Enviromental Science and Development).

Flores, I., K. Sobolev, L. M. Torres-Martinez, E. L. Cuellar, P. L. Valdez, and E. Zarazua. 2010. "Performances of Cement Systems with Nano-SiO2 Particles Produced by Using the Sol-Gel Method." (Transportation Research Board of the National Academies).

Flores-Vivián, Ismael , and Konstantin Sobolev. 2015. "The Effect of Nano-SiO2 on Cement Hydration." In *Nanotechnology in Construction*, 167-172. Springer.

Gaitero, J., I. Campillo, and A. Guerrero. 2008. "Reduction of the calcium leaching rate of cement paste by addition of silica nanoparticles." *Cement and Concrete Research* (Cement and Concrete Research) 1112–1118.

Garnier, Andre , Jean-Benoit Laudet, Nadine Neuville, Yvi Le Guen, Dominique Michael Fourmaintraux, Noureddine Rafai, Nicolas Burlion, and J.F. Shao . 2010. "CO2-Induced Changes in Oilwell Cement Under Downhole Conditions: First Experimental Results." *SPE.*

Godec, Michael, George Koperna, Robin Petrusak, and Anne Oudinot. 2013. "Assessment of Factors Influencing CO2 Storage Capacity and Injectivity in Eastern U.S. Gas Shales." *Energy Procedia* 37: 6644-6655.

Griffin, Andrew S., Muhammad K. Rahman, Jung J. Kim, and and Mahmoud Reda Taha. 2013. "The Significance of Nano Silica on Degradation of Oil Well Cement in Carbonated Brine Environments." In *Mechanics and Physics of Creep, Shrinkage, and Durability of Concrete*, 372-379.

He, Xiaodong, and Xianming Shi. 2008. "Chloride Permeability and Microstructure of Portland Cement Mortars Incorporating Nanomaterials." (Transportation Research Board of the National Academies).

Ilesanmi , Oluwagbemiga Ralpheal. 2013. "Long-term Wellbore Isolation In A Corrosive Environment." *SPE.*

Jain, Jitendra, and Narayanan Neithalath. 2009. "Analysis of calcium leaching behavior of plain and modified cement pastes in pure water." *Cement and Concrete Composites* 31 (3): 176-185.

Jafariesfad, Narjes , Mahmoud Khalifeh, Pål Skalle, and Mette Rica Geiker. 2017. "Nanorubber-modified cement system for oil and gas well cementing application." *Journal of Natural Gas Science and Engineering* 91-100.

Kannan, V. 2018. "Strength and durability performance of self compacting concrete containing self-combusted rice husk ash and metakaolin." *Construction and Building Materials* 160: 169-179.

Karim, R, M.F.M Zain, M Jamil, and N Islam. 2011. “Strength of concrete as influenced by palm oil fuel ash.” *Australian Journal of Basic and Applied Sciences* 990-997.

Kawashima, Shiho , Pengkun Hou , David J. Corr , and Surendra P. Shah. 2013. "Modification of cement-based materials with nanoparticles." *Cement and Concrete Composites* 8-15.

Khankhaje, Elnaz, Warid Mohd Hussin, Jahangir Mirza, Mahdi Rafieizonooz, Mohd Razman Salim, Ho Chin Siong, and Muhammad Naqiuddin Mohd Warid. 2016. “On blended cement and geopolymer concretes containing palm oil fuel ash.” *Materials & Design* 385-398.

Khanzadi, Mostafa, Mohsen Tadayon, Hamed Sepehri, and Mohammad Sepehri. 2010. "Influence of Nano-Silica Particles on Mechanical Properties." *Second International Conference on Sustainable Construction Materials and Technologies.*

Khalifeh, Mahmoud, Hem Bahadur Motra, Arild Saasen, and Helge Hodne. 2018. "Potential utilization for a rock based geopolymer in oil well cementing." *ASME 2018 37th International Conference on Ocean, Offshore and Artic Engineering.* Madrid: ASME.

Kim, S., and B.E. Dale. 2004. "Global potential bioethanol production from wasted crops and crop residues." *Biomass Bioenergy* 361-375.

Kong, Deyu , Xiangfei Du, Su Wei, Zhang Hua , Yang Yang, and Surendra P. Shah. 2012. "Influence of nano-silica agglomeration on microstructure and properties of the hardened cement-based materials." *Construction and Building Materials* 37: 707–715.

Kontoleontos, F. , P.E. Tsakiridis, A. Marinos, V. Kaloidas, and M. Katsioti. 2012. "Influence of colloidal Nano Silica on ultrafine cement hydration: Physicochemical and microstructural characterization." 35: 347–360.

Kosmatka, Steven H., Beatrix Kerkhoff, and William C. Panarese. 2003. *Design and Control of Concrete Mixtures.* Portland Cement Association, Skokie, Illinois, USA, 2003.

Kurdowski, Wieslaw. 2014. *Cement and Concrete Chemistry.* Springer.

Kurtis, Dr. Kimberly. 2007. "Portland Cement Hydration."

Kutchko, Barbara G., Brian R. Strazisar, David A. Dzombak, Gregory V. Lowry, and Niels Thaulow. 2007. "Degradation of Well Cement by CO2 under Geologic Sequestration Conditions." *Enviormental Science & Technology* 4787-4792.

Kutchko, Barbara G. , Brian R. Strazisar, Gregory V. Lowry, David A Dzombak, and Niels Thaulow. 2008. "Rate of CO2 Attack on Hydrated Class H Well Cement under Geologic Sequestration Conditions." *Environ. Sci. Technol* 6237-6242.

Le, H.T. 2015. "Behaviour of Rice Husk Ash in Self-Compacting High Performance Concrete." Weimar: Bauhaus-Universität Weimar, F.A. Finger- Institut für Baustoffkunde, Professur Werkstoffe des Bauens.

Lesti, M. , C. Tiemeyer, and J. Plank. 2013. "CO2 stability of Portland cement based well cementing systems for use on carbon capture & storage (CCS) wells." *Cement and Concrete Research* 45–54.

Lim, Seungmin, and Paramita Mondal. 2015. "Effects of incorporating Nano Silica on carbonation of cement paste." *Journal of Materials Science* (J Mater Sci) 3531-3540.

Maeda, N., I. Wada, M. Kawakami, T. Ueda, and G.K.D. Pushpala. 2001. "Development of a New Furnace for the Production of Rice Husk Ash." *The Seventh CANMET / ACI International Conference on Fly ash, Silica Fume, Slag and Natural Pozzolans in Concrete.* Chennai.

Mamlouk, Michael S., and John P. Zaniewski. 2011. *Materials for Civil nd Construction Engineers.* Pearson.

Marchetti, Cesare. 1977. "On geoengineering and the CO2 problem." *Climatic Change* 1 (1): 59-68.

Mehta, P.K. 2002. "Greening of the concrete industry for sustainable development." *Concrete International* 24 (7): 23-28.

Mindess, Sidney, J. Francis Young, and David Darwin. 2003. *Concrete.* Prentice Hall, Pearson Education, Inc.

2012. *Nano Work.* December 17. Accessed June 09, 2016. http://www.nanowerk.com/spotlight/spotid=28101.php.

Nair, Deepa G, Alex Fraaij, Adri A.K. Klaassen, and Arno P.M. Kentgens. 2008. "A structural investigation relating to the pozzolanic activity of rice husk ashes." *Cement and Concrete Research* 38 (6): 861-869

Nelson, E.B. 1990. *Well Cementing .* Schlumberger Educational Service.

Nygaard, R.,. 2010. "Well Design and Well Integrity." *Energy and Environmental System Group.*

Oyejobi, D. O., T. S. Abdulkadir, and V. M. Ajibola. 2014. “Investigation of Rice Husk Ash Cementitious Constituent in Concrete.” *International Journal of Agricultural Technology* 10 (3): 533-542.

Oyejobi, D. O., T. S. Abdulkadir, and A. T. Ahmed. 2015. “A Study of Partial Replacement of Cement with Palm Oil Fuel Ash in Concrete Production.” *Journal of Agricultural Technology* 12 (4): 619-631.

Peach, Jocelyn , and Julian Eastoe. 2014. "Supercritical carbon dioxide: a solvent like no other." *Beilstein Journal Of Organic Chemistry* 1878-1895.

Poppe, Anne-Mieke , and Geert De Schutter. 2005. “Cement hydration in the presence of high filler contents.” *Cement and Concrete Research* (Cement and Concrete Research) 35 (12): 2290–2299.

Rahman, Muhammad Kalimur, Sami Abdulkarem Amer, and Abdulaziz Abdalla Al-Majed. 2015. Portland cement type-g with Nano Silica additive for high pressure-high temperature applications. Patent US20150260009 A1. September 17.

Raza, Arshad , Reza Rezaee, Raoof Gholami, Vamegh Rasouli, Chua Han Bing, Ramasamy Nagarajan, and Mohamed Ali Hamid. 2015. "Injectivity and quantification of capillary trapping for CO2 storage: A review of influencing parameters." *Journal of Natural Gas Science and Engineering* 26: 510-517.

Riahi, Shadi , and Ali Nazari. 2011. "Compressive strength and abrasion resistance of concrete containing SiO2 and CuO nanoparticles in different curing media." *Science China Technological Sciences* 2349-2357.

Rukzon, Sumrerng , and Prinya Chindaprasirt. 2009. "An Experimental Investigation of the Carbonation of Blended Portland Cement Palm Oil Fuel Ash Mortar in an Indoor Environment." *SAGE journals.*

Safiuddin, Md. , Md. Abdus Salam, and Mohd Zamin Jumaat. 2011. "Utilization Of Palm Oil Fuel Ash In Concrete: A Review." *Journal Of Civil Engineering And Management* 17 (2): 234-247. doi:10.3846/13923730.2011.574450.

Salas, A., S. Delvasto, and R. Mejía de Gutiérrez. 2013. "Developing high-performance concrete incorporating highly-reactive rice husk ash." (INGENIERÍA E INVESTIGACIÓN) 33 (2): 49-55.

Salehi, Saeed , Mohammad Jamal Khattak, Nasir Ali, C. Ezeakacha, and Fatemeh K. Saleh. 2018. "Study and Use of Geopolymer Mixtures for Oil and Gas Well Cementing Applications." *Journal of Energy Resources Technology.*

Santra, Ashok Kumar , B.R. Reddy, Feng Liang, and Rocky Fitzgerald. 2009. "Reaction of CO2 With Portland Cement at Downhole Conditions and the Role of Pozzolanic Supplements." *SPE.*

Santra, Ashok Kumar, Peter Boul, and Xueyu Pang. 2012. "Influence of Nanomaterials in Oilwell Cement Hydration and Mechanical Properties." *SPE.*

Scrivener, K.L., T. Füllmann, E. Gallucci, G. Walenta, and E. Bermejo. 2004. "Quantitative study of Portland cement hydration by X-ray diffraction/Rietveld analysis and independent methods." *Cement and Concrete Research* 34 (9): 1541-1547.

Shah, Surendra P., Pengkun Hou, and Xin Cheng. 2015. "Durability of Cement-Based Materials and Nano-particles: A Review." In *Nanotechnology in Construction*, 15-24. Springer.

Singh, L.P. , S.K. Bhattacharyya, S.P. Shah, G. Mishra, and Sharma U. 2015. "Studies on early stage hydration of tricalcium silicate incorporating silica nanoparticles: Part I." *Construction and Building Materials* 943-949.

Singh, L.P. , S.R. Karade, S.K. Bhattacharyya, M.M. Yousuf, and S. Ahalawat. 2013. "Beneficial role of Nano Silica in cement based materials – A review." *Construction and Building Materials* 1069-1077.

Singh, L.P., D. Ali, and U. Sharma. 2016. "Studies on optimization of silica nanoparticles dosage in cementitious system." *Cement and Concrete Composites* 60-68.

Singh, L.P., S.K. Bhattacharyya, S.P. Shah, and U. Sharma. 2015. "Studies on Hydration of Tricalcium Silicate Incorporating Silica Nano-particles." In *Nanotechnology in Conctruction*, edited by Pengkun Hou , Xin Cheng Surendra P. Shah, 151-159.

Smith, D.K. 1990. *Cementing.* SPE.

Soares, Lech W.O., Renata M. Braga, Julio C.O.Freitas, Rafael A. Ventura, Dennys S.S. Pereira, and Dulce M.A. Melo. 2015. "The effect of rice husk ash as pozzolan in addition to cement Portland class G for oil well cementing." *Journal of Petroleum Science and Engineering* (Journal of Petroleum Science and Engineering 131: 80-85.

Sobolev, Konstantin. 2015. "Nanotechnology and Nanoengineering of Construction Materials." In *Nano Technology in Construction*, 3-15. Springer.

Sonebi, Mohammed, Patrick Carr, and Y. Ammar. 2015. "Effect of Nano-silica on Fresh Properties and Rheology of Grouts." In *Nanotechnology in Construction*, 187-192.

Sooraj , V.M. 2013. "Effect of Palm Oil Fuel Ash (POFA) on Strength Properties of Concrete." *International Journal of Scientific and Research Publications* 3 (6). Springer.

Subhashini, L, and A. Krishnamoorthi. 2016. “Experimental investigation on partial replacement of cement by palm oil fuel ash in concrete.” *International Journal of Advanced Research Trends in Engineering and Technology* 3 (4): 44-48.

Sudendro, B. 2014. "Toward green concrete for better sustainable enviorment." *2nd International Conference on Sustainable Civil.*

Sukantapree, S., C. Namarak, and C. Jaturapitakkul. 2002. “Use of calcium carbide residue and palm oil fuel ash in concrete.” *Proc. of the annual conference of the engineering Institute of Thailand.* 191-199.

Sumadi, S.R., and M.W. Hussin. 1995. "Palm oil fuel ash (POFA) as a future partial cement replacment material in housing construction." *Journal of Ferrocement* 25-34.

Tangchirapat, Weerachart , Jatupol Tangpakasit, Saksin Waew-kum, and Chai Jaturapitakkul. 2003. “A NEW POZZOLANIC MATERIAL FROM PALM OIL FUEL ASH.” *KMUTT Research & Development Journal* 459-473.

Tay, J.H. 1990. “Ash from oil-palm waste as concrete material.” *Journal of Materials in Civil Engineering* 94-105.

Thomas, Blessen Skariah. 2018. "Green concrete partially comprised of rice husk ash as a supplementary cementitious material – A comprehensive review." *Renewable and Sustainable Energy Reviews* 82 (3): 3913-3923

Timmer, C.P., Steven A Block, and David Dawe. 2010. "Long-run dynamics of rice consumption, 1960-2050." *Rice in the Global Economy: Strategic Research and Policy Issues for Food Security* 139.

Tonnayopas, D., F. Nilrat, K. Putto, and J. Tantiwitayawanich. 2006. "Effect of oil palm fiber fuel ash on compressive strength of hardening cement." *Proceedings of the 4th Thailand Materials Science and Technology Conference.* Pathumthani, Thailand. 1-3

Toews, Karen L. , Robert M. Shroll, Chien M. Wai, and Neil G. Smart. 1995. "pH-Defining Equilibrium between Water and Supercritical CO2. Influence on SFE of Organics and Metal Chelates." *Analytical Chemistry* 4040-4043.

Van, Viet-Thien-An, Christiane Rößler, Danh-Dai Bui, and Horst-Michael Ludwig. 2013. "Mesoporous structure and pozzolanic reactivity of rice husk ash in cementitious system." *Construction and Building Materials* 43: 208-216.

Verba, C., and W. O'Connor. 2010. "CO2-alteration rates for Class H Portland cement." *9th Annual Conference on Carbon Capture and Sequestration.* Pitsburgh. 10-13.

Xu, W., T.Y. Lo, and S.A. Memon. 2012. "Microstructure and reactivity of rich husk ash." *Construction and Building Materials* 29: 541-547.

Ye, G., X. Liu, G. De Schutte, A.-M. Poppea, and L. Taerwe. 2007. "Influence of limestone powder used as filler in SCC on hydration and microstructure of cement pastes." *Cement and Concrete Composites* 29 (2): 94–102.

Zareeia, Seyed Alireza, Farshad Ameri, Farzan Dorostkar, and Mojtaba Ahmadi. 2017. "Rice husk ash as a partial replacement of cement in high strength concrete containing micro silica: Evaluating durability and mechanical properties." *Case Studies in Construction Materials* 73-81.

Zhang, M.H., and V.M. Malhotra. 1996. "High-performance concrete incorporating rice husk ash as a supplementary cementing material." *ACI Mater* 629-639.

Zhang , Min , and Stephen Talman. 2014. "Experimental Study of Well Cement Carbonation under Geological Storage Conditions." *Energy Procedia* 5813-5821.

Zhang, Liwei , David A. Dzombak, David V. Nakles, Steven B. Hawthorne, David J. Miller, Barbara Kutchko, Christina Lopano, and Brian Strazisar. 2014. "Effect of exposure environment on the interactions between acid gas (H2S and CO2) and pozzolan-amended wellbore cement under acid gas co-sequestration conditions." *International Journal of Greenhouse Gas Control* 309-318.

Zhang, Ming, and Stefan Bachu. 2011. "Review of integrity of existing wells in relation to CO2 geological storage: What do we know?" *International Journal of Greenhouse Gas Control* 5 (4): 826-840.

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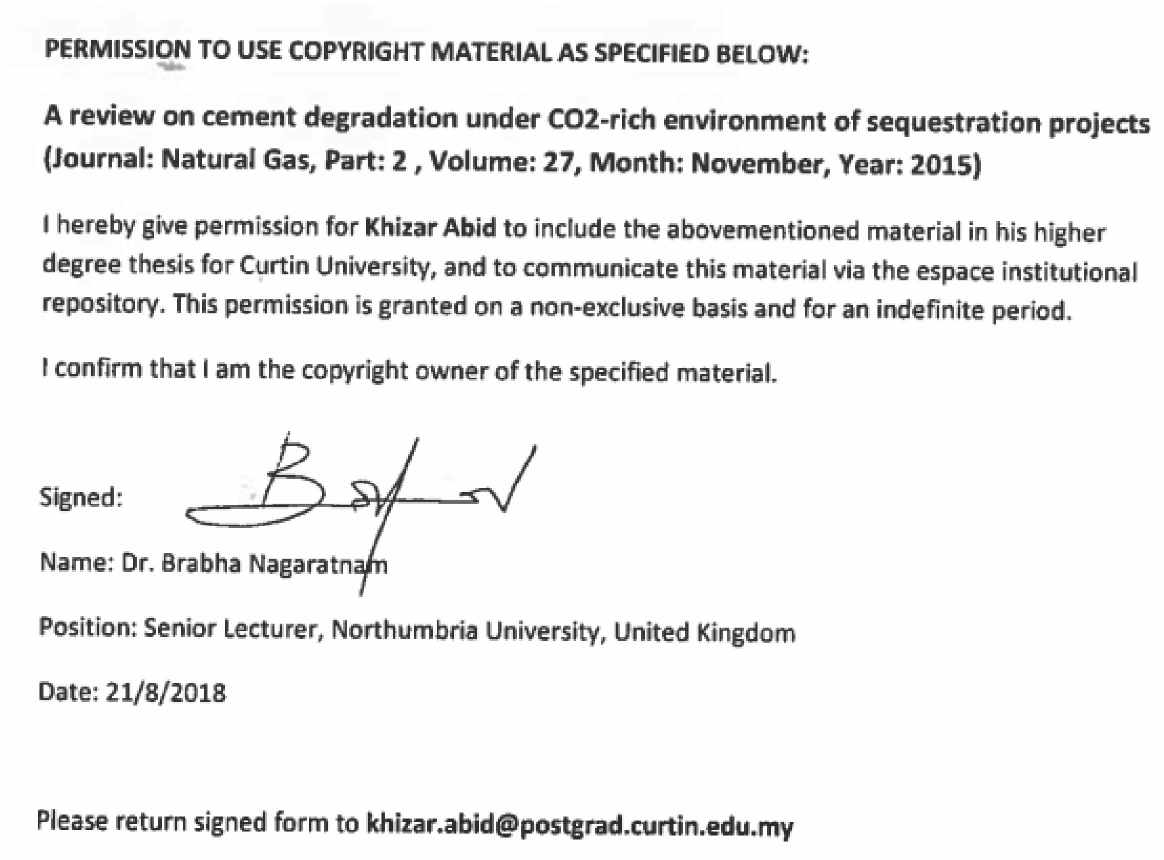

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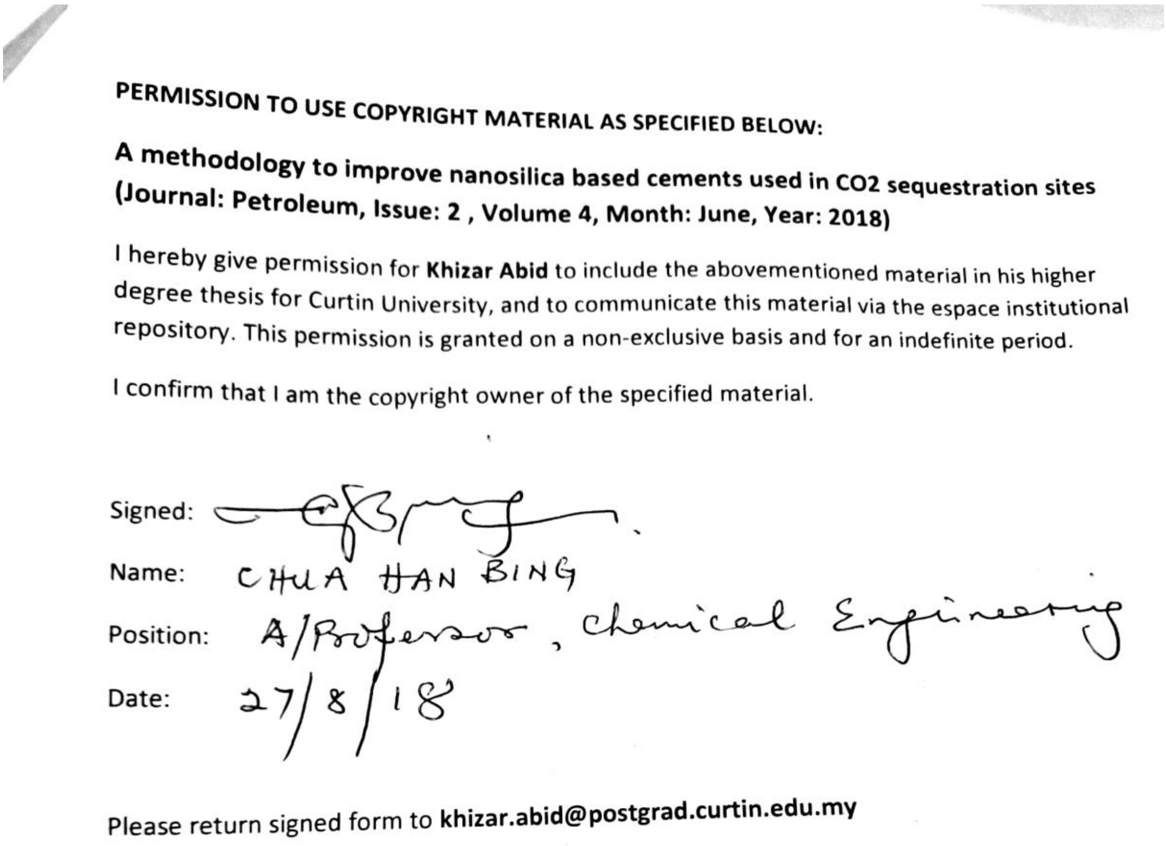

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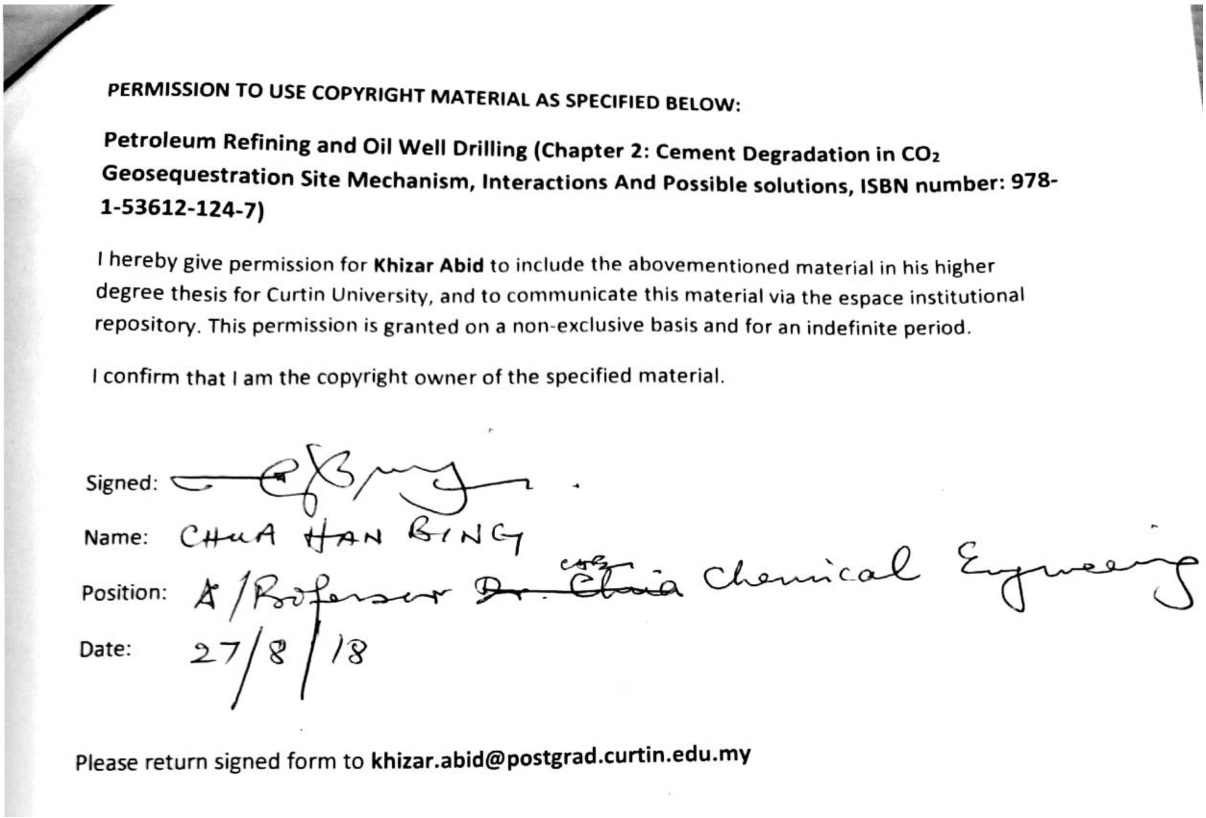

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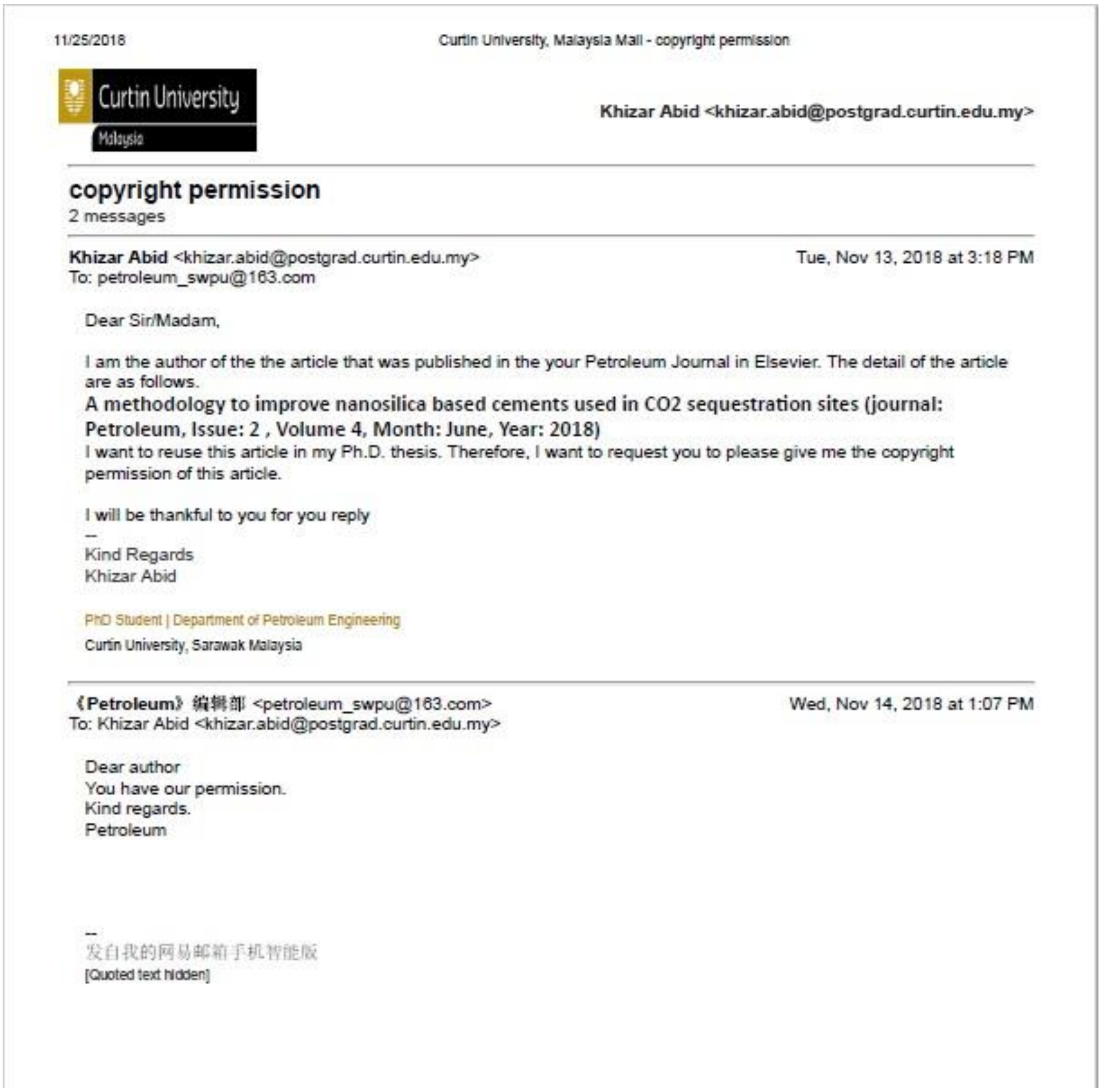

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