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Effect of MWCNT/SiO_2 nanoparticles and Salinity on the thermo-mechanical property of G-Class Portland Cement

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Abstract

This paper reports the impact of multi-walled carbon nanotube (MWCNT) and silicon dioxide (SiO_2) nanoparticles and salinity on the thermo-mechanical and internal pore structure behavior of G-class Portland oil well cement. Nanoparticle blended cement plugs strength were measured after 7 and 28 days of curing.

Results showed that the effect of nanoparticles and salinity on conventional slurry vary nonlinearly as the concentration and the degree of salinity changes. In seawater blended cement, addition of 0.026-0.26 % by weight of cement (bwoc) increased the uniaxial compressive strength by over 26%. Similar improvement is also observed in deionized water based slurry system. In seawater/fresh mixture, addition of 0.13%bwoc SiO_2 increased the tensile strength of cement significantly. MWCNT has little to no effect on exothermic reaction process.

1 Introduction

In an oil and gas well, cement is one of the vital barrier elements used during well construction, completion and abandonment phases. During well construction phase, cement fills the annular spacing between the open hole and casing in order to provide well structural integrity, prevent formation fluids leakage and hence control potential casing corrosion. However, the performance of cement is determined by a good cement job and qualities of cement slurry. The properties of cement slurry and its behavior depend on the composition of the additives.

According to NORSOK D-010 standard, for the cement to act as a permanent well barrier it should have properties such as impermeable, non-shrinkage, provide long-term integrity (eternal perspective), ductile (not brittle), able to withstand mechanical loads/impact, resistant to chemicals/ substances (H_2S, CO_2 and hydrocarbons), have good wetting to ensure bonding to steel and not harmful to the steel tubulars integrity

[1]. However, the conventional cement slurry shows defects and does not completely satisfy the NORSOK D10 requirement.

Vignes and Aadnøy [2] have examined the integrity status of the Norwegian Continental Shelf (NCS) wells based on the information obtained from 7 operators. Out of the considered 75 injection and production wells, the integrity survey result among others showed that 11% problems were associated with cement. Through cement bond logging, (Watson and Bachu, 2009) [3] reported cement channeling, which was due to poor cement bond job and the resulting casing corrosion was investigated in several Alberta's wells.

Several researchers have experimentally investigated the micro-sized mineral admixture effect on ordinary cement and achieved a significant cement property improvement [4-7]. Moreover, in the recent years, the performance of nanotechnology (1-100 nm) on cement properties have shown impressive results and its application becomes attractive for the oil & gas industry. Nanomaterials create improved materials through chemical and/or physical processes. The effect of nanoparticles on material properties depends on several factors such as its size, shape, surface chemistry and concentration. Nanoparticle provides a higher surface area-to-volume ratio [8]. Due to the reduced size, the resulting exceptional large surface area and changes within the surface chemistry, surface morphology and surface energy, nanoparticles exhibited positive impacts on the internal structure, mechanical, elastic and other properties of cement. Some of the reviewed research results on cementing systems include TiO_2 [9-14], $CaCO_3$ [15], SiO_2 [16-19], graphene oxide [20, 21]. MWCNT [22, 23] carbon nanotubes (CNT) [24], and MgO [25]

Along with SiO_2, MWCNT is the main focus of this paper. Just to have a closer look at earlier research results, the work presented by Rehman et al. (2016) [23] is summarized. The authors have experimentally investigated the effect of MWCNT on compressive strength and rheological properties (plastic viscosity, yield stress and gel strength) of oil well cement slurries. Results showed that treating the conventional cement with 0.1%, 0.25% and 0.5% CNT by weight of cement, the compressive strength of the cement increased with 19%, 10% and 9%, respectively. Similarly, the effect of the additives has shown impacts on the rheological properties nonlinearly with respect to concentration.

Patil et al. (2012) [26] studied the effect of silica nanoparticle on Premium Class H Cement with respect to strength, rheology in the presence of fluid loss control additives (Latex). Test result showed that the nanoparticle improved early strength development, ultimate strength, and fluid loss significantly.

However, up to the knowledge of the authors not much research has been done the synergy of MWCNT and SiO_2 with salinity on the microstructure and bulk properties of an oil well cement.

In this paper, the effect of MWCNT blended with multi- and single salt systems on the hydration, microstructure and mechanical properties of cement was studied by means of hydration heat, scanning electron microscope (SEM), water absorption, and destructive and non-destructive test methods. Moreover, the impact of SiO_2 and their composites with MWCNT were tested.

2 Theory

Cement plugs were characterized through mechanical destructive (Uniaxial and Brazilian- tensile) and non-destructive (Ultrasonic) test methods. Combining these two different test datasets, an empirical model will be developed and tested with other measured data.

2.1 Non-Destructive test (Ultrasonic Velocity)

Before the mechanical testing, the strength development and elasticity were evaluated through the non-destructive test method. Ultrasonic velocity measures the materials ability to transmit sonic waves. **Figure 1** illustrates the wave propagation through the core plug.

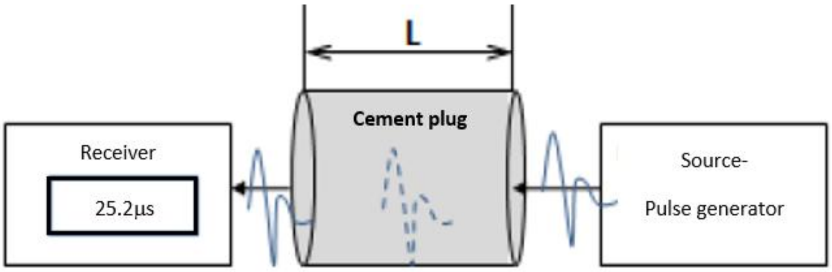


Figure 1: Sonic wave propagation through core plug

The compressional wave velocity can be calculated from the travel time and the length through which the wave propagates as:

$$V_p = \frac{L}{t} \quad (1)$$

Where

- V_p is the velocity,
- L is the specimen length and
- t (µs) is sonic wave travel time.

2.2 Destructive tests (UCS & TS)

After 7 and 28 days, the mechanical strength of the core plugs have been tested with uniaxial compressive (**Figure 2**) and Brazilian (**Figure 3**) destructive test methods. The plug specimen is placed centrally between the two parallel steel plates and a load is continuously applied until the plug fails.

Uniaxial compressive test measures the strength of a material to carry the maximum load before it is being failed by shear. The uniaxial compressive strength (UCS) is calculated as: [27]:

$$UCS = \frac{F_{max}}{A} \qquad 2$$

Where

- F_{max} is the maximum load carrying capacity of the plugs and
- A is the cross-sectional area of the specimen

Brazilian test measures the tensile strength (TS) of the rock, which is the measure of the splitting resistance of rock specimen. Unlike steel, rock is weak in tensile strength. The tensile strength of the rock is commonly determined indirectly from Brazilian test. Using the maximum tensile load obtained from the experiment and from the geometry of the core plug, the tensile strength is estimated as: [27]

$$TS = \frac{2F_{max}}{\pi DL} \qquad 3$$

Where

- F_{max} is the maximum load carrying capacity of the plugs,
- D is the diameter and
- L is the length of the core plug.

Figure 2: Uniaxial compressive test

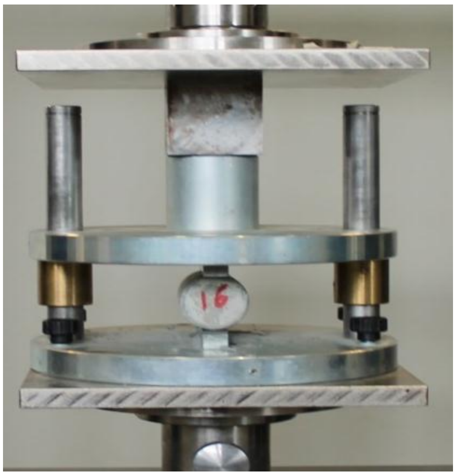


Figure 3: Brazilian test setup

3 Experimental works

In this section, the effect of MWCNT, SiO_2 and their composite on the Portland cement control (reference) are presented. The control cement mortar was formulated with cement and synthetic brine, Seawater, Deionized and Tap water. Using destructive and non-destructive testes outlined in section 2, the impact of nanoparticle on the control slurry were investigated at room temperature. Finally, the modelling and test part will be demonstrated.

3.1 Materials and Methods

3.1.1. Materials

Portland oil well cement used for the experiment and was supplied by NORCEM Co., Ltd. (Stavanger, Norway), which is highly sulfate resistance and tested in accordance with API SPEC 10A/NS-EN ISO 10426-1 [28]. The chemical composition and the physical properties are provided in **Table 1** and **Table 2**. Nanoparticles used in this paper, MWCNT with average diameter 20-40nm and SiO_2 with an average diameter of 20nm were obtained from EPRUI Nanoparticles & Microspheres Co. Ltd, (Beijing, China) [29]. The characterization of the particles is shown in **Table 3** and **4**, respectively. The composition of the synthetic brines & Seawater used in this study are provided in **Table 5.**

Table 1: Physical properties of Portland cement. [28]

Density (lb/gal)	Surface Area (m^2/kg)	Max. Consistency Bc	Thickening time Min
16	317	13	108

Table 2: Chemical compositions of Portland cement. (*I.R = Insoluble residue) [28]

Cr(VI)	SO_3	C_3A	C_2S	C_4AF+ $2C_3A$	Na_3O	MgO	I.R*	Loss on Ignition
0.00	1.73%	1.7%	55.6%	15.2%	0.48%	1.43	0.1%	0.79%

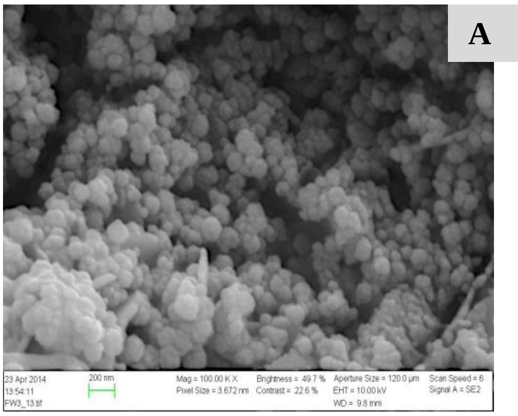
Table 3: Characterization of the used MWCNT. [29]

Appearance	OD Particle Size (nm)	ID Particle Size (nm)	Length (μm)	Purity %	Surface Area (m^2/g)	Density (g/cm^3)	Electrical conductivity s/cm
Black powder	20-40	5-10	10-30	>95	>80	2.1	>100

Table 4: Characterization of the used Silica [29]

Appearance	Mean Particle Size (nm)	Purity %	pH	Surface Area (m^2/g)	Density (g/cm^3)	Morphology
White powder	20	>99.5	4–7	300	0.10	Spherical

The morphology of silica and MWCNT has been analyzed by scanning electron microscopic (SEM) observation. Silica showed in Figure 4a is spherical shape (**A**) and the MWCNT is fiber like structure (**B**).



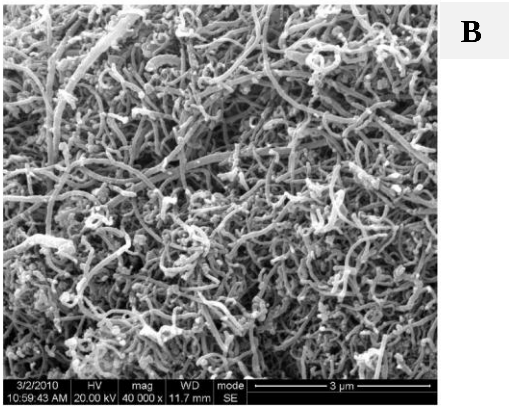


Figure 4: Scanning electron microscopic (SEM) of (A) Silica; (B) MWCNT

Brine systems (Synthetic water and Sea water)

Seawater was fetched from Stavanger harbor, which is part of the North Sea. The chemistry and composition are provided in **Table 5a** [30]. Based on the chemistry of formation water in Texas, a multi-salt based synthetic brine was mixed [31]. **Table 5b** shows the salt composition of th**e s**ynthetic water (SYW) comprises of 31.1g/L

Ions	mol/l	ppt	wt%
HCO_3^-	0.002	0.12	0.37
Cl^-	0.525	18.61	55.74
SO_4^{-2}	0.024	2.31	6.90
Mg^{+2}	0.045	1.09	3.28
Ca^{+2}	0.013	0.52	1.56
Na^+	0.450	10.35	30.98
K^+	0.010	0.39	1.17
Total		33.39	100

Table 5a: Composition of Seawater.

Salt	Salt content gr/L
$NaHCO_3$	15,6
Na_2SO_4	7,30
NaCl	3,86
Na_2CO_3	3,3
$MgSO_4$	0,62
$CaSO_4$	0,42
Total	**31,1**

Table 5b: Composition of synthetic water.

3.1.2. Preparation of Cement Mortar

Table 6 shows the 0.51 water/cement ratio (WCR) mortar mix proportions along with nanoparticle. The reference cement slurry was formulated by mixing 191g Portland cement with 100g Water (Tap water (FW), Deionized (DI), Seawater (SW) and Synthetic brine water (SYW)). Nanoparticle treated slurries were formulated by mixing nanoparticles with the reference mortar system. During mixing process, we prefer to use hand mixing in order not to separate the nanoparticles out of the solution. We have observed such condition when mixing with Hamilton beach high speed mixer. Several test matrixes have been designed. The first phase of the test was to investigate the effect of various salinity in on cement treated/untreated with 0.26 % MWCNT by weight of cement (bwoc). After selecting the best brine-fresh water system, the second phase was to investigate the effect of nanoparticle concentration in the range of 0.026wt %-0.26 wt. % bwoc.

Table 6: Mix proportions of cement mortar

Slurry	Composition
Reference cement (0.51 WCR)	191 Portland Cement + 100gm Water
Nanoparticle based cement	Reference cement + (0.026-0.26%) bwoc nanoparticles

3.1.3 Testing Procedures

In this experiment, the different MWCNT & SiO$_2$ nanoparticle treated pastes were immediately poured into a 70 mm height × 36 mm diameter cylindrical cup. Then the samples were cured at 20 ± 1 °C. After 48 hrs, the specimens were immersed in water during the curing process. The non-destructive tests have been measured every 24 hrs. Finally, after 7-and 28 days, the plugs have been mechanically crushed with uniaxial compressive and Brazilian test machines.

4 Results and discussion

4.1 Effect of Salinity and MWCNT concentration

The effect of 0.26% bwoc MWCNT on cement blended with 10% synthetic water, which is 10% of each salt provided in **Table 5a** (i.e. 3.11g/l). The idea is to reduce the ions in the cement slurry so that one can avoid/reduce the possible corrosion effects on the casing. A total of 13 plugs have been formulated by mixing the 10% SYW with tap water. After conducting non-destructive test, it was found that the 80% of the 10%SYW mixed with 20% Tap water showed a higher value of the modulus of elasticity. The fluid systems have been selected to study the effect of nanoparticle concentration.

The effect of MWCNT concentration was investigated in Seawater (SW) and Deionized water (DI). **Table 7** and **Table 8** provide the additives, respectively. **Figure 5a** and **Figure 5b** show the uniaxial test load-deformation and the computed uniaxial compressive strength, respectively. As shown in the figures, except for nanoparticle free slurry (i.e. SW_0), all nanoparticle treated systems carried a load up to the machine's limit (i.e. 20000N). This indicates that the nanoparticle system could carry more than 20kN. Comparing with the reference SW_0, the considered nanoparticle concentrations increased the UCS by over 26%. Similarly, **Figure 6a** and **Figure 6b** show the test results obtained from Deionized water system. As shown, all the nanoparticle additives improved the uniaxial compressive strength of the reference slurry (i.e. DI_0). The 0.1 and 0.26 % wt. bwoc reached to the maximum load limits improving the strength by about 26%.

Plug #	SW_0	SW_1	SW_2	SW_3	SW_4	SW_5
MWCNT (% bwoc)	0	0.05	0.1	0.16	0.21	0.26

Table 7: Cement slurry prepared with Seawater (SW)

Plug #	DI_0	DI_1	DI_2	DI_3	DI_4	DI_5
MWCNT (% bwoc)	0	0.05	0.1	0.16	0.21	0.26

Table 8: **Cement slurry prepared with Deionized water (DI)**

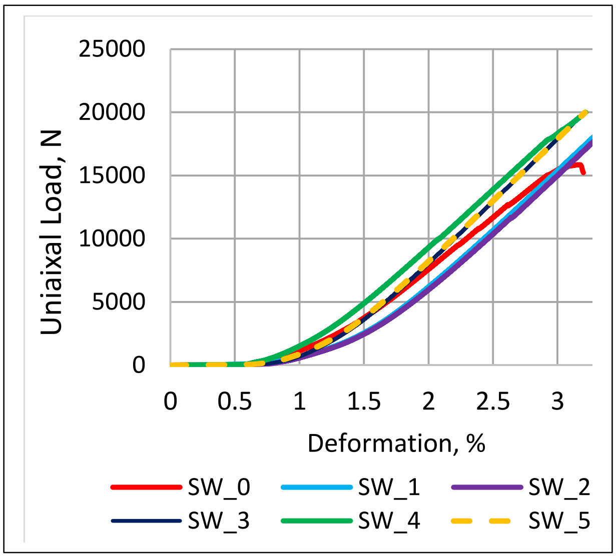


Figure 5a: Uniaxial compressive load on SW based plugs

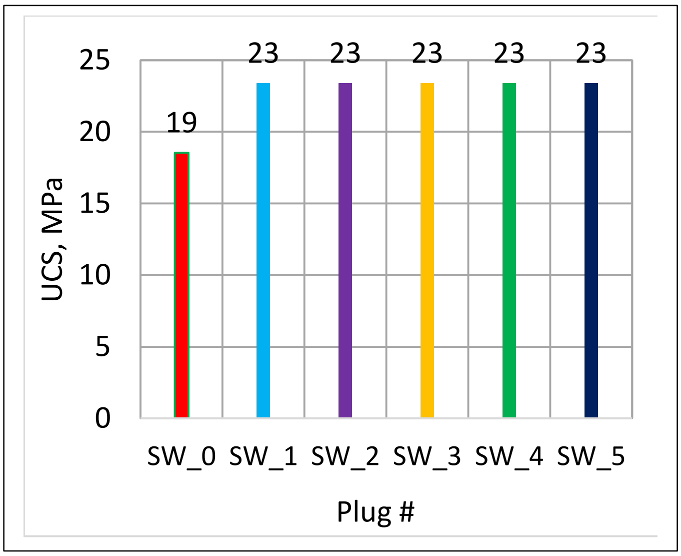


Figure 5b: Uniaxial compressive strength SW based plugs

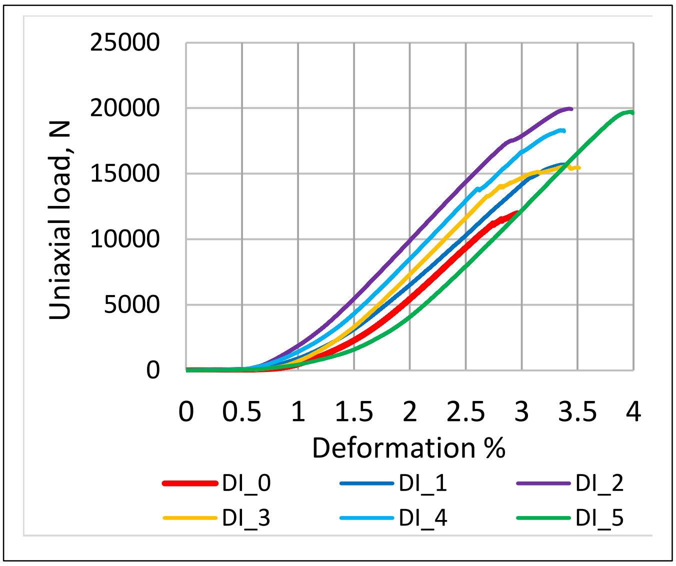


Figure 6a: Uniaxial compressive load on DI based plugs

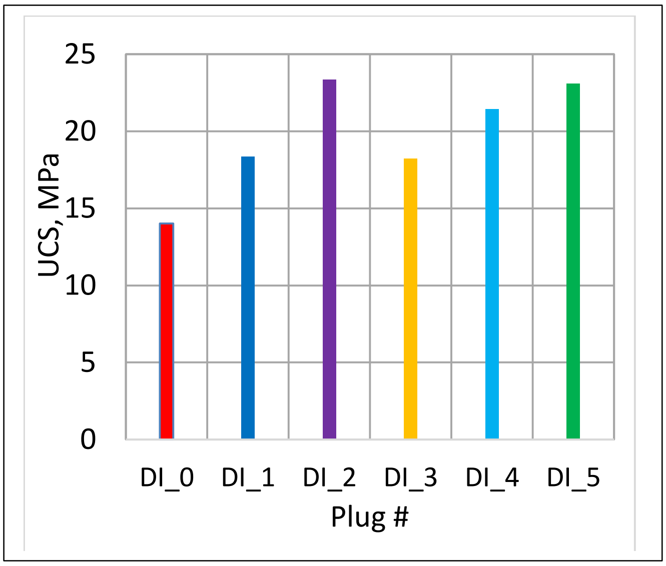


Figure 6b: Uniaxial compressive strength DI based plugs

In the absence of nanoparticle, the effect of the four different water system's chemistry on cement strength were evaluated and the results are displayed in **Figure 7a** and **7b**. The ionic composition of synthetic brine water (SYW) is provided in Table 5a, but 10% of each salt were mixed per liter of tap water (i.e. 3.11 g/l). For instance, comparing the SYW system with the tap water and the de-ionized water based cement, it is shown an increase in the UCS by about 15% and 64%, respectively. On the other hand, the UCS of cement treated with SW is higher than the Deionized based cement by 26.3%. Similar effect is also observed in the presence of nanoparticles (see Figure 5a/b and Figure 6a/b). The result indicates how salinity plays important role on the strength of cement.

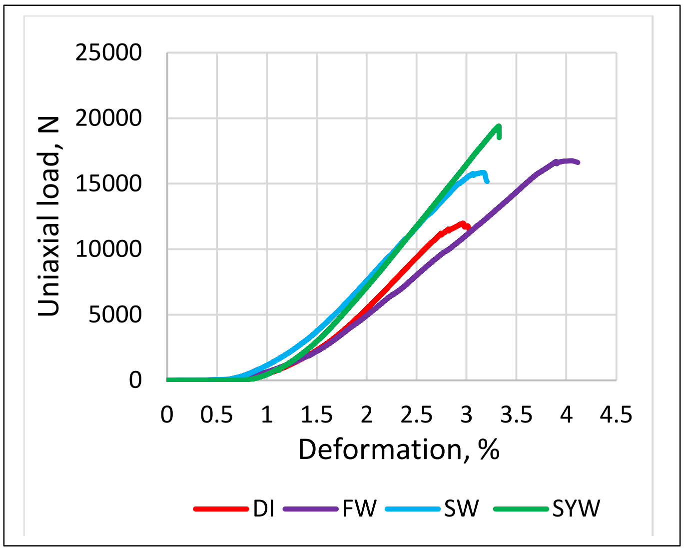


Figure 7a: Uniaxial compressive load on DI, FW, SW and SYW plugs

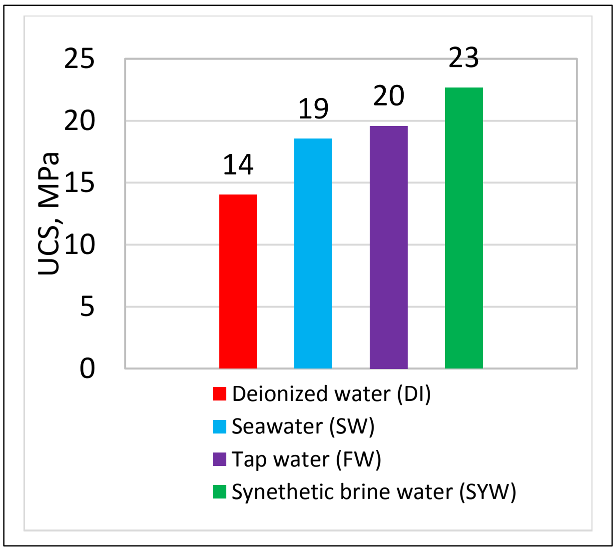


Figure 7b: Uniaxial compressive strength DI, FW, SW and SYW plugs

4.1.2 Heat of hydration

As cement powder mixes with water, an exothermic chemical reaction that releases energy by heat takes place. The process is commonly known with the term "hydration" [32]. During the hydration process, cement fluid interaction passes through different phases such as water adsorption on the surface of the cement and the dissolution of inorganic phases. Moreover, new silicate and aluminate hydrated phases is responsible for the binding of cement. In this phase, cement is an amorphous calcium silicate hydrate, called C-S-H, having the properties of a rigid gel. Further, the hydration process follows as crystalline $Ca\,(OH)_2$. There are several techniques to assess the heat of hydration and one of them is using a calorimeter. However, due to the unavailability of measuring equipment and since the exothermic heat development process is directly related with the temperature, in this paper we measured the transient temperature evolution during the 41 hrs period. For the evaluation of heat development, 0.05%, 0.16% and 0.26% bwoc MWCNT concentration of nanoparticles and brine have been selected based on the best result obtained from the uniaxial compressive strength test.

During testing, one liter cement slurry was placed in 10cmx10cmx10cm sized insulated polystyrene boxes to isolate the slurry from the laboratory room temperature. The slurry's temperature history was logged with temperature sensors and the memory data downloaded with Easy Log software. **Figure 8** shows the test result. The data logging was every five minutes. Among the considered additives, it is likely that the 0.26 bwoc % might have a quick instantaneous initial exothermic reaction during the first stage. As time went by, one can also observe temperature development until reaching to the maximum peak of 56^{o}C and cooling down gently in time. For instance, the 0.26% bwoc MWCNT additive increased the peak temperature by 0.9% as compared with the nanoparticle free slurry. One can also observe a non-linear effect with respect to concentration. However, more studies are required to come to a conclusion. Please note that Href (0g MWCNT) on the legend means a reference slurry without nanoparticle and Href (0.5 g MWCNT) means the reference slurry was treated with 0.5 g MWCNT.

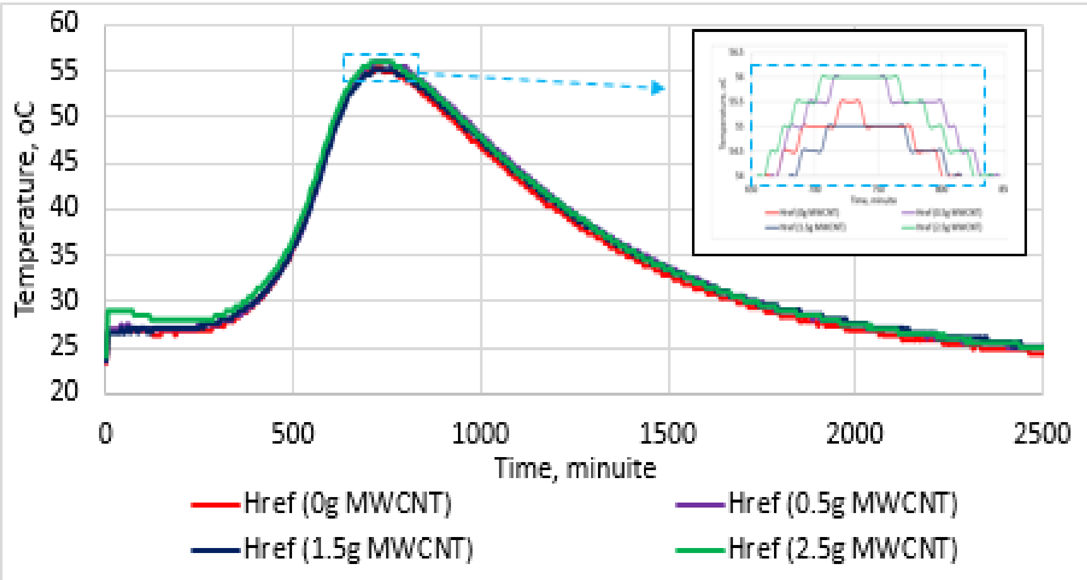


Figure 8: Heat of hydration

4.2 Effect of Salinity and SiO_2concentration

Here the effect of salinity and SiO_2concentration on the cement was evaluated by measuring the tensile strength of cement plug specimens. Table 8 shows the fluid and nanoparticle concentrations used in the 0.51WCR cement plugs. P1 and P5 are nanoparticle free reference plugs, which were formulated from 50/50% Seawater (SW)/Freshwater (FW) and 80/20% Seawater (SW)/Freshwater (FW), respectively. The rest of the plugs (P2-P4) were blended with 0.13-0.39%bwoc SiO_2 in the 50/50%

SW/FW-fluid system. Likewise, plugs (P6-P8) were mixed in the 80/20 SW/FW blended brine and nanoparticles [33]**.** As displayed in **Figure 9,** the test results in both fluid systems show that the 0.13bwoc% SiO_2 nanoparticle system exhibited a significant impact on the tensile strength. However, increasing the concentration, the tensile strength shows decreasing. The result also indicates that the performance of SiO_2 is a nonlinear function of concentration and depends on the salinity of the fluid system as well. The optimum concentration can be determined through experimental testing.

Fluid/SiO_2	P1	P2	P3	P4	P5	P6	P7	P8
SW, %	50	50	50	50	80	80	80	80
FW, %	50	50	50	50	20	20	20	20
SiO_2, %bwoc	0	0.13	0.26	0.39	0.0	0.13	0.26	0.39

Table 8: Cement slurry prepared SiO2 and SW/FW mixture [33]

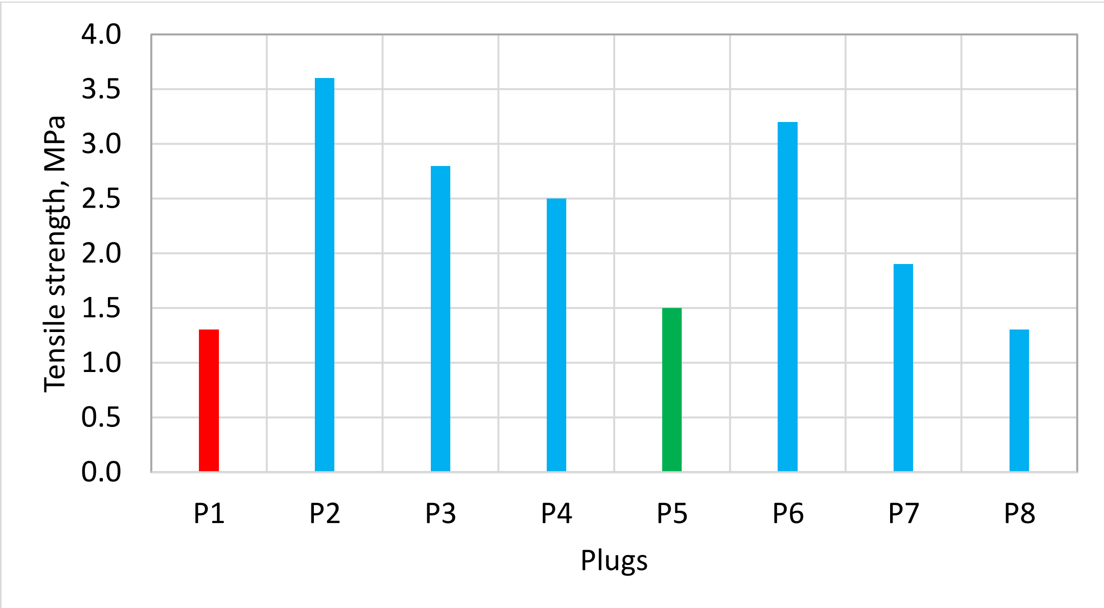


Figure 9: Effect of SiO_2 concentration and salinity on tensile test [33]

4.3 Effect of MWCNT-SiO_2 composite

In the previous section, it is shown the single nanoparticles performance on cement strength. To investigate the effect of MWCNT and SiO_2 composite, cement treated with the best SYW, which was selected based on the non-destructive modulus of elasticity analysis. The composition of the SYW comprises of 20% SYW (i.e. 3.11g/l) and 80% Tap water (FW). The salt concentration of the fluid system would be 0.622 g/l. **Table 9** shows the test matrix (TM), where TM_0 is nanoparticle free system and the rest are nanoparticles composite (TM_1-3) and the single nanoparticle systems (TM_ MWCNT and TM_SiO_2). The nanoparticle additives is 0.16%bwoc.

Type	Plug (#)	Fluids		Nanoparticles		
		SYW (g)	**FW (g)**	**MWCNT (g)**	**SiO_2 (g)**	**% bwoc**
Reference	TM_0	20	80	0	0	0
MWCNT-SiO2 composite **(Figure 10)**	TM_1			0.05	0.25	0.16
	TM_2			0.15	0.15	
	TM_3			0.25	0.05	
Single Nanoparticle **(Figure 11)**	TM_MWCNT			0.3	0	
	TM_SiO_2			0	0.3	

Table 9: Cement plug specimens

Figure 10 displays the comparison between the control specimen and the nanoparticle composite treated plugs. The results show that the 1:1 ratio nanoparticle composite increased the UCS by about 14.6%. On the other hand, as shown in **Figure 11**, the single SiO_2 increased the UCS by 18% and the MWCNT don't show any impact. The reason for the performance mechanism up this level of research is not yet investigated. However, among others the effect could be due to the chemistry of nanoparticles interaction with the considered fluid systems and also the degree of dispersion when mixing the slurry.

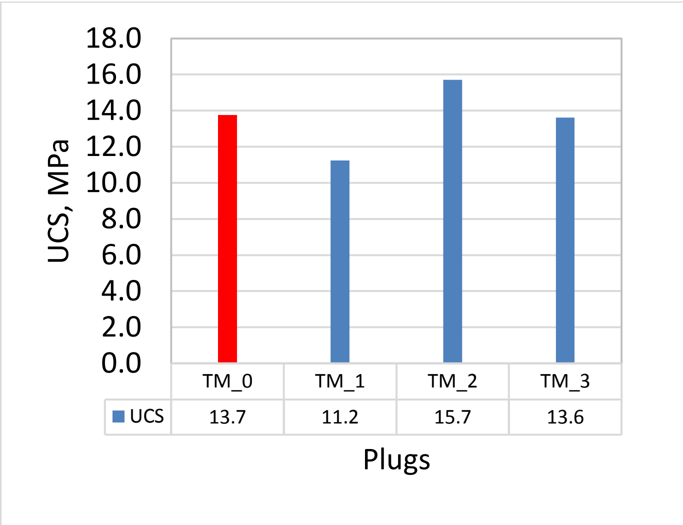


Figure 10: Effect of MWCNT-SiO2 composite on cement

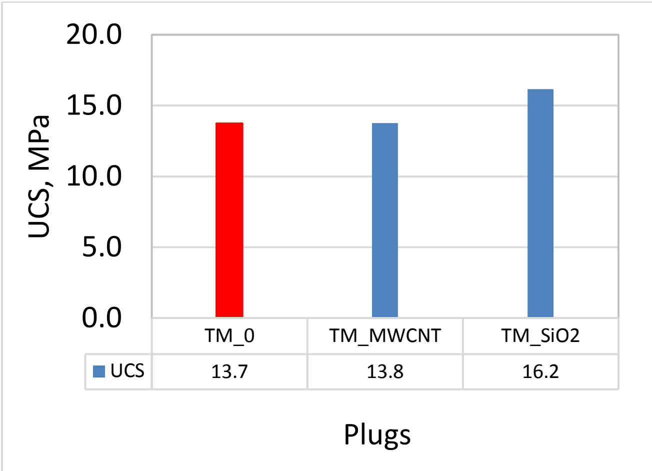


Figure 11: Effect of single MWCNT and SiO_2 on cement

4.4 Analysis of internal structure

The internal structure of the 0.26wt %bwoc MWCNT treated cement plug was analyzed through the scanning electron microscope (SEM) image and the elemental dispersion spectroscopy (EDS). As shown in the SEM picture, **Figure 12a,** the aggregated nanoparticle embedded in the pore structure and its EDS analysis as shown in **Figure 12b** comprises of high concentration of carbon, with little impurities. Since the slurry has been mixed by hand, one can observe poor dispersion of MWCNT nanoparticle in the system and the quantity was also insufficient in the bulk volume. The green circle on the figure indicated pore spaces where nanoparticle is not fill out. Very well dispersed slurry might distribute the nanoparticle uniformly in the system and hence improve the pore filling performance of the nanoparticle. Moreover, it may have a significant impact on the strength.

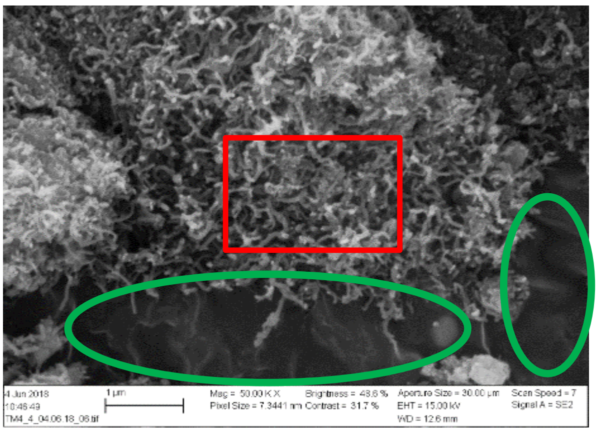
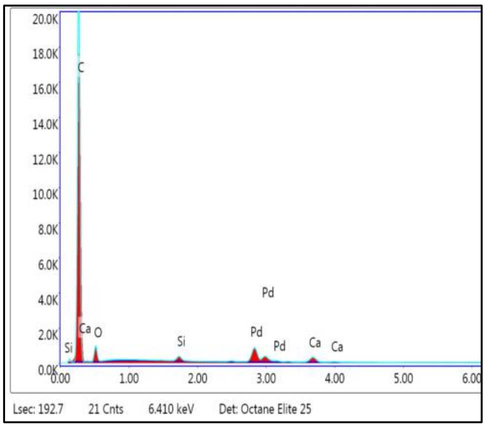



Figure 12a: SEM Picture sporting at MWCNT Figure 12b: EDS-analysis of the MWCNT

5 New model development

There are several empirical models available that relates UCS with V_p. Among others Horsrud's model [34], which was developed from sedimentary rock (i.e. shale). The model reads:

$$UCS(MPa) = 0.77Vp^{2.92} \quad 4$$

Where, V_p is compressional wave velocity in km/s.

The Horsrud's model (Eq. 4) was used to compare with our experimental data. Results showed poor prediction with significant deviation as shown in Figure 14. Therefore, using on our experimental data, new empirical UCS-V_p model was developed. As displayed in **Figure 13,** the best fit model with R^2 = 0.9738 reads:

$$UCS(MPa) = 2\, e^{0.65\,Vp} \quad 5$$

Where V_p is in km/s

Figure 14 shows the comparisons between equations 4 and 5 with experimental test data. As shown, the model prediction (Eq. 5) is quite good with minor deviation. The applicability of the model further needs to be tested on more other cement related and sedimentary rock-based dataset.

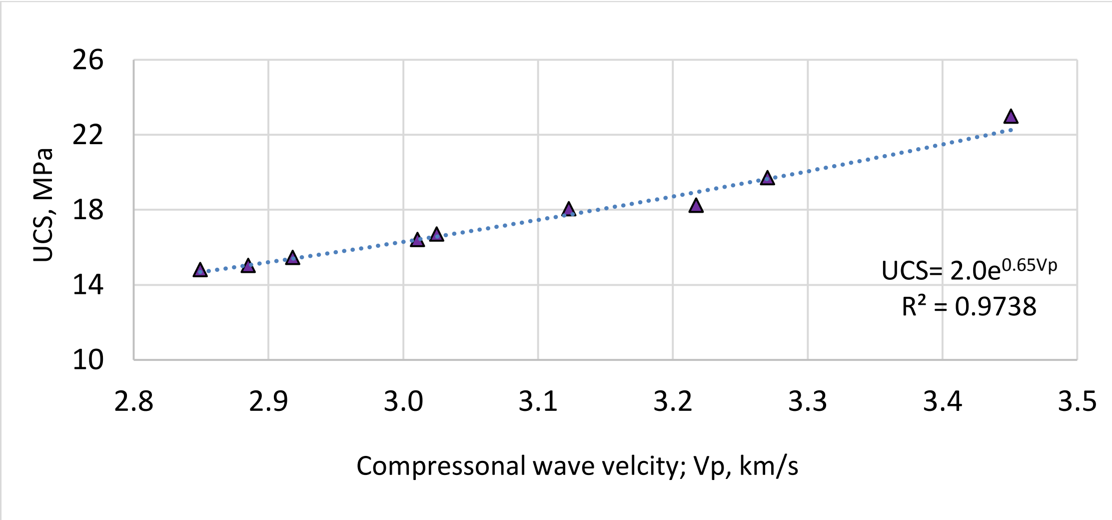


Figure 13: New UCS-V_p empirical model

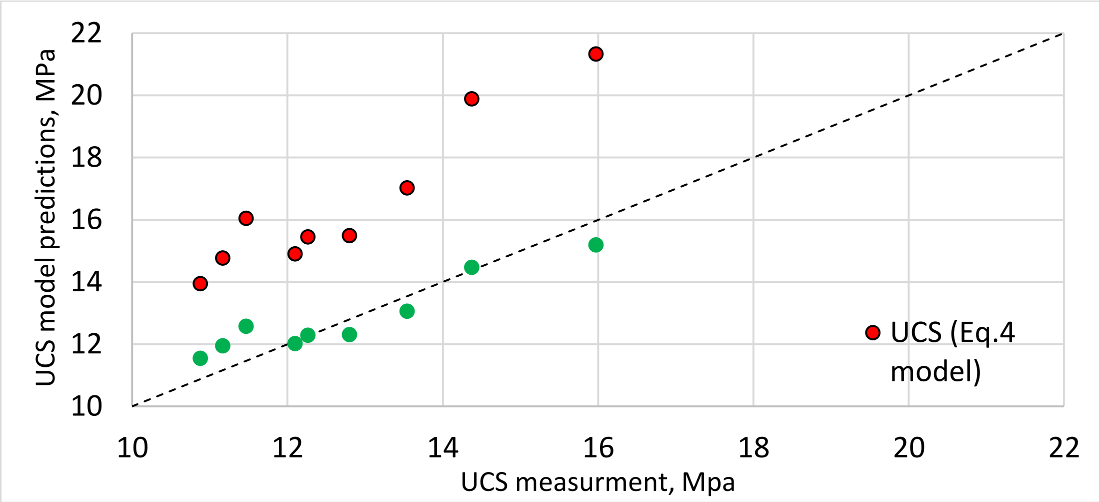


Figure 14: Comparison between model prediction (Eq.4, Eq.5) and measurement

6 Summary

In this paper, the performance of the single and composite of MWCNT & SiO_2 nanoparticles was experimentally evaluated in Tap water, Seawater, Deionized and synthetic brine water. One clear observation is that the impact of nanoparticles depends on its concentration, type and fluid salinity.

Results based on the considered reference systems can be summarized as follows:

- MWCNT increased the mechanical strength of cement in Seawater and Deionized, but the effect is very significant in SW.
- Addition of 0.13%bwoc SiO_2 improves the tensile strength, but as the strength deceases as the concentration increases.
- In nanoparticle free system, cement treated with selected synthetic brine showed a higher UCS.
- Addition of 0.05-0.26%bwoc MWCNT did not show any thermal effect.
- Out of the 0.16%bwoc MWCNT-SiO_2 composite, the 1:1 ratio showed an improved result. However, the performance varies in different fluid systems.

Please note that changing the composition of the reference slurry with respect to concentration and salinity, one may get different results. However, the result presented in this paper indicated how salinity and nanoparticle types and concentration have impact on cement. For the application purpose, it is important to conduct several experiments under the given environmental conditions such as temperature and pressure.

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