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The effect of Silicon dioxide (SiO_2) Nanoparticle on the Tensile strength of Cement Slurry

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ABSTRACT

In the recent years, research results have shown that nanoparticles improve the properties of conventional cement. In this paper, the effect of Silicon Dioxide (SiO_2) nanoparticle on G-class cement treated with seawater, freshwater and their mixture have been evaluated through experimental studies. The results, among others, in 50:50 seawater-fresh mixture treated cement slurry show that:

- The addition of 0.25wt% Nano-SiO_2 increases the tensile strength by 170% as compared with the nano free system and the additive also shows less effect on the rheology
- However, as the concentration of Nano-SiO_2 increases from 0.25wt% to 0.5wt% and 0.75 wt%, the tensile strength shows decreasement and the cement slurry becomes more viscous.

The overall experimental analysis shows that the 0.25wt% Nano-SiO_2 was found out to be the best and optimized based system in the considered cement slurry systems.

1 INTRODUCTION

Cement is one of the crucial elements used during well-construction process. Among other functions, cement fills annular spacing between casing & wellbore, provides structural integrity and prevents fluid migration to surface. NORSOK-D10 standard defines the required cement properties. These are that cement should be impermeable, long term integrity, non-shrinkage, ductile not brittle, resistance to different substances and wetting to ensure bonding [1].

However, the integrity survey in the Norwegian continental shelf (NCS) showed cement related problems, which is also the case in other part of the world. Poor cement job or poor quality of cement reduce well integrity. These form channeling, which can allow formation fluid to flow axially to the surface and laterally communicating formation fluid and casing. Formation fluid, which contains brine, is a corrosive environment and results in casing corrosion. The 2006 well integrity survey from NCS wells study showed 11% cementing and 11% casing failure out of the considered production and injection wells [2].

This shows the need to improve the mechanical, elastic and petro-physical properties of conventional oil well cement.

Nanotechnology (1nm -100 nm) is a promising technology in solving technical challenges that the conventional technology could not solve. Nanomaterials have the ability to create materials with improved properties through chemical and/or physical processes. These properties include among others thermal, mechanical, electrical, and rheological properties, which depend significantly on size and shape of the nanoparticles. The surface area to volume ratio of the nano-system is significantly higher than the micro/macro sized particles (Amanullah et al, 2009) [3]. Due to the small size, nanoparticles form a tough, dense mud cake and seals off micro cracks in shale (Riley et al, 2012) [4]. A potential for fluid loss reduction with the use of nanoparticles in drilling fluid is documented in Charles et al, 2013 [5], Sharma et al, 2012 [6], katherine et al, 2012[7].

The effect of an engineered microsized cement improves packing of cement system and improves the sealing performance of vent flows Farkas et al (1900) [8], Slater et al (2001) [9]. Similarly, the positive effect of nano particles on cement slurry properties has been documented in several papers among others Rahul et al., (2012) [10] Roji et al. (2012) [11] Jeremiah et al. (2012) [12]Ershadi et al. (2011) [13] Patil et al. (2012) [14] Li, H. et al (2003) [15] Rahimirad et al. (2012) [16] Patil, et al.'s (2012,) [17] Santra et al. (2012) [18], Rui et al. (2015)[19]

2 THEORY

The knowledge of the mechanical, elastic, petrophysical and the physical properties of cement is important for the design of loading carrying capacity. These parameters determine the workability of the cement for a given loading and environmental conditions

Cement failure mechanisms are either by shear or tensile. When the hoop/tangential stress reaches to the tensile strength, cement fails by tensile mode and creates fracture. This allows formation fluid to communicate with casing. This loading induced channeling is also another mechanism for casing corrosion and loss of well integrity. Therefore, in this paper the tensile strength of cement plugs were tested.

Mechanically, rocks and cement in oil wells are weak in tension. A Brazilian test is an indirect test method developed to determine the tensile strength of a cement plug. As shown on **Figure 1**, a cylindrical cement specimen is placed between two parallel plates. During testing, the load (P) is applied in the axial direction until the plug fails. The tensile strength was then calculated using equation 1: [20]

$$\sigma_t = \frac{2P}{\pi D L} \quad (1)$$

Where, σ_t is the tensile strength (Pa), P is the applied force that cause sample to break (N) , D is the sample's diameter (m), and L is the sample's length (m).

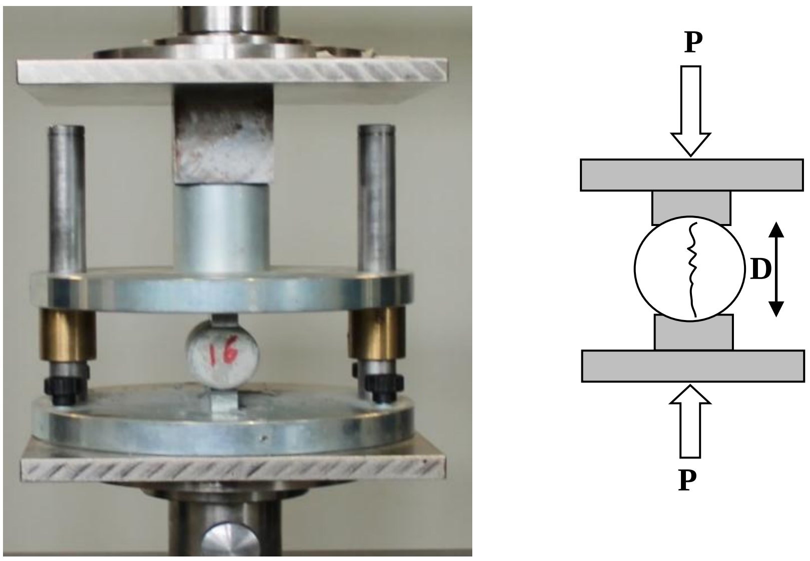

Figure 1: An illustration of Brazilian test on a cylindrical cement plug specimen

The dynamic modulus of elasticity of the plugs have been estimated from the measured compressional sonic measurement and density using Eq. 2. [20]

$$M = K + \frac{4}{3}G = 10^{-9}\, V_p^2 . \rho \quad (2)$$

Where, M is the modulus of elasticity (GPa), K is the Bulk modulus (GPa), G is the shear modulus (GPa), V_p is the P-wave velocity (m/s), and ρ is the density (kg/m^3).

3 EXPERIMENTAL INVESTIGATION

As mentioned earlier, the purpose of the study is to evaluate the effect of Nano-SiO_2 in various saline fluid systems with respect to the tensile strength and rheology. This section presents the material (Nano particle, Salinity of fluid systems) descriptions, cement slurry and plug preparation, and the measured test results.

3.1 Materials characterization

3.1.1 Silica dioxide nanoparticle

For experimental investigation, 15nm sized SiO_2 was used. The particles were purchased from a Chinese company [21]. Since a detailed specification of the particles was not received, a characterization of the structure and a elemental identification was performed using Scanning Electron Microscopy (SEM) and Elemental Dispersive Spectroscopy (EDS). **Figure 2a** and **Figure 2b** show the SEM image and EDS element analysis, respectively. Based on **Figure 2b,** one can observe the purity of the Nano-SiO_2. Please note that the palladium (pd) is not a part of the Nano particle.

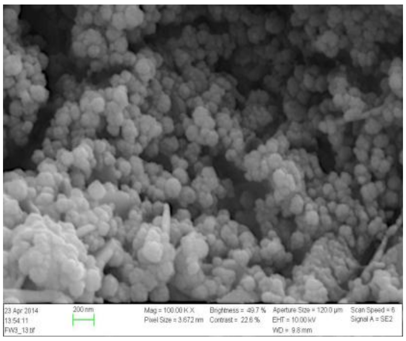

Figure 2a: SEM picture of Nano-SiO_2.

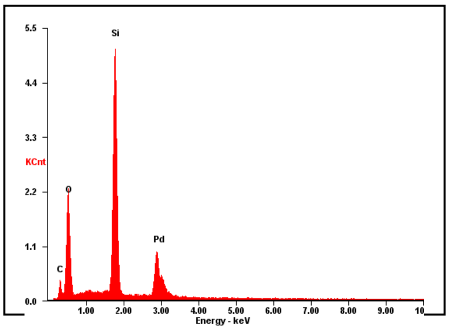

Figure 2b: Element analysis

3.1.2 Fluid systems

Cement slurries were formulated using seawater (SW), freshwater (FW) and their mixture. Fresh water used was tap water and the ionic composition of the fluid was not analyzed. The SW was obtained from the Stavanger harbor, which is part of the North Sea. Salinity of a fluid describes the amount of dissolved salts in a fluid, and is usually given in ppt (parts per thousand). Seyed Farzad [22] analyzed the SW salinity and ions concentrations. **Table 1** shows the amount of various salt ions in the SW in moles per litre, ppt and percentage. The total salinity of the SW is 33.39 ppt. The composition of SW shows that the primary salt ions are chloride (Cl^-) and Sodium (Na^+), which makeup almost 87% of all the salt.

Table 2 provides the fluid systems used for the formulation of cement slurry. Using the measured resistivity and Shlumberger Chart 9 [23], the salinity of the fluids was estimated. Since seawater was fetched from the surface of the sea, the one estimated here is not the same as the one reported in reference [24]. The difference could mainly be due to (1) salt precipitation, (2) the chart does not perfectly predict the measurement and/or (3) uncertainty in measurement of resistivity. However, the main objective of the estimation was to analyze the resistivity trend of the various fluid mixtures. As shown in **Table, 2**, the salinity increases with increasing amount of seawater. However, the pH is not influenced significantly. The pH values are alkaline, just above the neutral value.

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 1: The composition of the salt in the seawater [24]

Seawater %	Freshwater %	pH	Resistivity (Ωm)	Salinity from Gen-9 (ppt)
100	0	7.55	0.30	22
90	10	7.75	0.32	20
80	20	7.85	0.32	20
70	30	7.85	0.36	18
60	40	7.90	0.37	17
50	50	7.75	0.42	15
40	60	7.70	0.48	13
30	70	7.65	0.60	10
20	80	7.65	0.76	8
10	90	7.65	1.11	5.5
0	100	7.35	21.0	<0.2

Table 2: Fluid system characterization

3.2 Core plug preparation and test results

3.2.1 Preparation of cement plugs

Several cement plugs have been prepared by mixing cement with fresh water, seawater and with their mixture as described in **Table 3.** The water-to-cement ratio (WCR) of the cement slurry was 0.52, and considered as a reference or Nano free. The Nano treated cement slurry was formulated by adding a certain weight percent of the total reference slurry. The slurry was very well mixed until homogenous and it was poured into a cylindrical plastic cup, having a diameter of 32.5 mm and a length of 70 mm.

3.2.2 Non-destructive test: Effect of salinity in 0.5wt% Nano-SiO_2 treated systems

A total of 13 Nano-SiO_2 free and treated cement plugs were prepared to study the effect of salinity on the elastic properties. First, non-destructive sonic test method was used to estimate the modulus of elasticity, which is the measure of stiffness and compressive strength of cement slurry. Based on the test results, two best slurry systems were selected for further Nano concentration effect study.

Plug number #	Seawater %	Freshwater %	Nano SiO2 wt%	Water-Cement ratio
1	100	0	0	0.52
2	100	0	0.5	0.52
3	90	10	0.5	0.52
4	80	20	0.5	0.52
5	70	30	0.5	0.52
6	60	40	0.5	0.52
7	50	50	0.5	0.52
8	40	60	0.5	0.52
9	30	70	0.5	0.52
10	20	80	0.5	0.52
11	10	90	0.5	0.52
12	0	100	0.5	0.52
13	0	100	0	0.52

Table 3: Test matrix for slurry formulation

The modulus of elasticity has been estimated by using Eq. 2 and the results are displayed on **Figure 3**. The sonic measurements have been made every 24hrs, for three days, after the plugs have been immersed in water. After 72hrs, it was observed that the water absorption process had stopped. Comparing the seawater plugs #1 and #2, the 0.5wt% Nano increased the modulus of elasticity by 0.3GPa, which is insignificant. On the other hand, comparing the fresh water plugs #12 and #13; the addition of 0.5wt% Nano increased the modulus of elasticity by 3.9GPa. These observations are for the considered Nano additive and will not be valid for other concentrations. Up to this level of research, the mechanism for the different impacts are not yet investigated. However, later the destructive test result will provide more information.

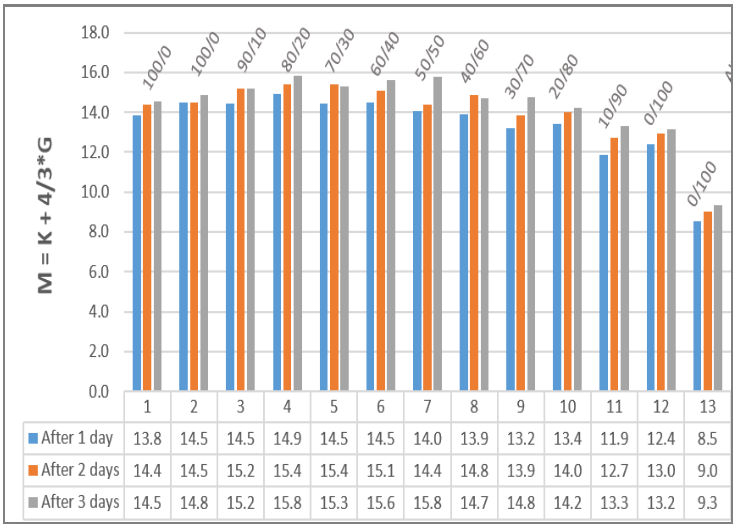

Figure 3: The elastic modulus for plugs #1 after 1, 2 and 3 days in water

3.2.3 Destructive-Tensile test: Effect of salinity in 0.5wt% Nano-SiO_2 treated systems

Brazilian destructive tensile test has been performed on the selected plugs formulated in **Table 3**. The selection was based on the modulus of elasticity displayed on **Figure 3.** The plugs are the 100% seawater (plug #1 and #2), the 100% fresh water (plug#12 and #13), and the combination of seawater and fresh water plugs (80/20, 70/30, 50/50 and 20/80). **Figure 4** shows the effect of 0.5wt% SiO_2 and salinity on tensile strength of cement plugs. As can be seen on the figure the 70/30 (plug#5) and the fresh water 0/100 (plug#12) show a relatively higher value than the other plugs. On the other hand, the seawater systems (plugs 100/0(plug#1 &2) and the 80/20 (plug#4)) exhibit lower values as compared with the fresh water. In the 100% fresh water system, as shown on plugs #12 and #13, the addition of 0.5wt% Nano-SiO_2 increased the tensile strength by about 17.5%. On the other hand, in the 100% seawater system, the addition of 0.5wt% Nano-SiO_2 increased the tensile strength by about 8.5%.

Furthermore, the test results obtained from the 70/30 SW:FW shows relatively comparable tensile strength to the Nano treated 100% FW system. Please note that this analysis is based on the 0.5wt% Nano-SiO_2 additive. The next part of the test results will provide more information on the effect of nano concentration.

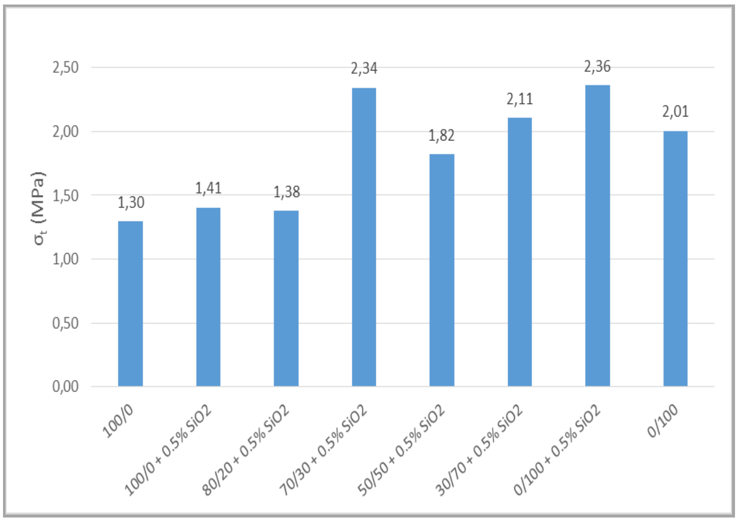

Figure 4: Effect of 0.5wt% SiO_2 and salinity on tensile test

3.2.4 Destructive-Tensile test: Effect Nano-SiO_2 concentration in 80:20 &50:50 ratio fluids

Based on the non-destructive results obtained from the 13 plugs (**Figure 3**), we can observe that plug #4 (80/20 + 0.5wt% Nano-SiO_2) and plug #7 (50/50 + 0.5wt% Nano-SiO_2) records a higher modulus of elasticity. However, the tensile strength test results showed that both plugs had lower values. In order to investigate the effect of Nano concentration, these two plugs were further considered. In addition to the concentration of 0.5wt% Nano-SiO_2, 0.25wt% and 0.75wt% was tested. **Figure 5** shows the effect of SiO_2 concentration and salinity on tensile strength of the cement plugs. Comparing the nano treated plugs in the 50/50 SW:FW fluid with the nano free system, one can observe that the 0.25wt% Nano-silica improved the tensile strength by +170%. Another observation is that as the nano concetration increases, the tensile strength decreases as compared with the 0.25wt%. However, the addition of 0.5wt% and 0.75wt% increases the tensile strength by +115% and +86% respectively.

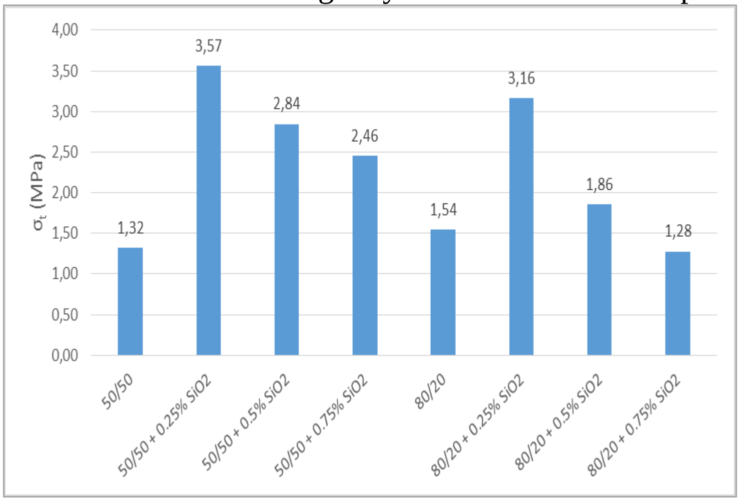

Figure 5: Effect of SiO_2 concentration and salinity on tensile test

Similarly, the analysis of the tensile strength in the 80/20 (SW:FW) system showed that the addition of 0.25wt% Nano-silica improved the tensile strength of the Nano free cement slurry by +105%. As Nano concentration increases to 0.5wt% and 0.75wt%, the tensile strength increased by +20% and reduced by -17%, respectively. In both seawater-freshwater mixed systems, 0.25wt% Nano-SiO_2 was found out to be an optimum and the best concentration. From the test results analysis, a clear observation is that the tensile strength is a nonlinear relation with Nano concentration. Reducing the concentration, one may get a better performance. For this, several test matrix should be designed and repeat tests need to be performed.

The Nano free cement slurry formulated in the 80/20 (SW/FW) plugs show higher tensile strength than the 50/50 (SW/FW) plug. On the other hand, the Nano-silica treated cement in the 50/50 (SW/FW) showed higher strength than 80/20(SW/FW) plug provided that the concentration of cement is the same amount. Furthermore, Nano-silica improved the 50/50 ratio cement much better than the 80/20 ratio cement.

3.3 Effect of Nano-SiO_2 additives on the rheology of cement slurry

Rheology is the study of deformation and flow of all types of matter. Before a cementing job, it is important to measure the rheological properties of cement slurry because it determine the pump pressure required and the well pressure in order to make sure that the well is not fractured during cementing [24]. There are several rheology models available in literature [25, 26]. Among others, Casson model is used for characterization of cement slurry. The Casson model is more accurate at both very high and very low shear rate. [26]. Like the Herschel-Bulkley, Casson model combines yield stress with shear-thinning behavior for $n < 1$ [25]. Casson rheology model is a two parameter model, which is described by yield stress and plastic viscosity. The yield stress describes an electrostatic attractive force of ions or charges between solids and solution. The viscosity describes the resistance of fluid flow. Casson rheology model is given as [25]:

$$\tau^{0.5} = \tau_c^{0.5} + \mu_c^{0.5}\gamma^{0.5} \qquad \text{For } \tau < \tau_c \qquad (3a)$$

$$\gamma = 0 \qquad \text{For } \tau \geq \tau_c \qquad (3b)$$

Where

τ is the shear stress (lbf/100 ft^2)
τ_c is the Casson yield stress ($lb_f/100ft^2$)

μ_c is the Casson plastic viscosity (lbf.s/100 ft^2)
γ is the shear rate (sec^{-1})

Figure 6 shows the measured viscometer data of the Nano free reference 100%SW, 100%FW and the mixed 50:50(SW:FW) ratio treated Nano-SiO_2. As the Nano concentration increases the viscometer response showed increase. The Nano free viscometer dial reading of the slurry in SW system is higher than in the FW system.

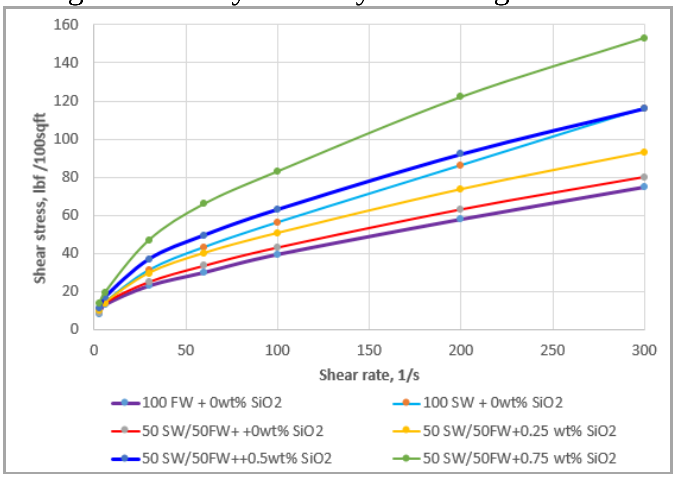

Figure 6: Viscometer response of nano and nano free cement slurry

Figure 7 shows the computed Casson yield stress. As shown, yield strength increased in the SW and FW mixture system as Nano-SiO_2 increases. The Nano free slurries showed relatively lower values. Based on the Brazilian test, the 0.25wt% additives showed higher tensile strength and increased the Casson yield strength by +10% as compared with the Nano free SW/FW mixture system

Figure 8 also shows the computed Casson plastic viscosity. In the SW/FW mixture system, as the Nano concentration increases the plastic viscosity increases. For instance, comparing the Nano free system with the 0.25wt%, the Nano SiO_2 increase the Casson plastic viscosity by +21%.

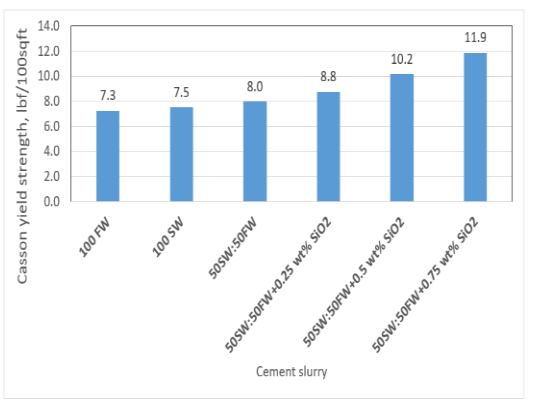

Figure 7: Casson yield strength of cement slurry.

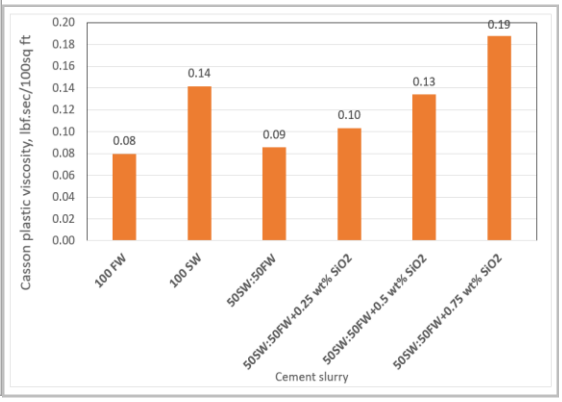

Figure 8: Casson plastic viscosity of cement slurry

4 SUMMARY

In this paper, the effect of various concentration of Nano-SiO_2 in fresh water, seawater and their combination. The rheology and the cement plugs have been tested.

One clear observation is that the performance of Nano-SiO_2 depends on its concentration, and fluid salinity. From the overall test results, the performance of Nano-SiO_2 summarized as follows:

- As Nano concentration increases, the viscometer response the cement slurry shows increament.
- The performance of SiO_2 varies as salinity of the fluid systems varies.
- In terms of tensile strength, the performance of Nano-SiO_2 is a nonlinear relationship.
- An optimum lower concentration Nano provides good performances. Increasing the concentration, the tensile strength becomes weaker and even weaker than the Nano free slurry.
- The effect of 0.5wt% Nano-SiO_2 is better in 100% FW than in 100% SW. However, reducing the concentration, one may get different result.
- Nano-SiO_2 shows better performance in SW/FW mixture.
- From the considered fluid system, the performance of 0.25wt% Nano was found out to be the best system in terms of tensile strength. The additive does not significantly influence the rheology of the slurry, and hence pumping pressure.

Please note that the above observations are based on the considered system. However, including different additives and changing the temperature/pressure states, one may get different behaviors.

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