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An approach to enhance the durability and mechanical properties of Class G cement using nano materials

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Abstract. Maintaining the integrity of the cement used to seal off the injection intervals of sequestrations sites is crucial to confine CO₂ for thousands of years. There have been many studies to resolve the issue of cement degradation induced in the presence of CO₂, but a very limited success has been reported to the application of the approaches proposed so far. Nano materials have gained the attention of many researchers in the past decade and might be able to resolve the issue of cement degradation given their outstanding performance and proven applications in the civil and polymer industries. In this paper, attempts are made to improve the physical and mechanical characteristics of class G cement using nano glass flakes (NGFs) and multiple-walled carbon nanotubes (MWCNTs). To do this, different cement-nanocomposites were prepared using two mixing techniques and their physical and mechanical changes were evaluated under different curing conditions. Samples with cylindrical shape of were prepared and cured under the temperature of 50°C and atmospheric pressure for 1 days. The results obtained indicated both nanoparticles are neutrally stable and may have a very slight effect on the cement rheology but may significantly increase the strength of the cement. It was concluded that the cement with 0.05 wt.% MWCNTs can provide the best results in terms of rheology, compositional changes and compressive strength.

Keywords. class g cement; nano glass flake; multiple-walled carbon nanotubes; CO₂ sequestration

1. Introduction

Oil well cementing is considered as one of the important activities for drilling operation as it determines the well sustainability. It is normally used to seal the annulus between the well casing and the formation rock. Based on the API Specification for Well Cementing 10A, typical wellbore cements are made of Ordinary Portland Cement, either class G or class H cements. Both of them are commonly used to seal off the injection intervals in carbon dioxide (CO₂) sequestration. Under these circumstances, cement is not only subjected to high pressure and high temperature condition of subsurface layers but also exposed to supercritical CO₂, which are favorable for cement degradation to take place. When cement degradation happens, the porosity and permeability of the cement will be increased, at the same time, the cement strength will be reduced [1].



To enhance the resistance of the cement, many studies were carried out but a limited success has been reported to the application of these approaches once tested in the field condition. One of the successful approaches which may work under these circumstances is the integration of nano materials with the cement, given the outstanding characteristics of nano material such as their aspect ratio and active surfaces. In this paper, two nano materials including nano glass flakes (NGFs) and multi walled carbon nanotubes (MWCNTs) were used to improve the physical and mechanical characteristics of Class G cement. These two nano particles were selected because of their outstanding performance reported in the earlier studies [2,3].

2. Materials and methods

Nano materials

NGFs are solid in the form of flakes which have a very smooth surface. They have a density around 2.4-2.8g/cm³ and a thickness of 75nm-100nm with a layered structure (See Figure 1) [4]. These layered structures would create tortuous pathways which prevent the outsiders to intrude into the substances [5, 6]. Since they are chemically inert and can withstand a high melting point, up to 930°C, they are competent to improve the designed cement of HPHT CO₂ sequestration sites. MWCNTs (Figure 2), on the other hand, they were chosen due to their extremely high mechanical, thermal and electrical properties. They appear as clumpy black powders with an extremely high melting point of 3652°C. Their densities are around 2.6g/cm³ and they are structurally rolled graphite sheets with the diameter of 1-2nm [7, 8].

Sample preparation

Class G cement without any additive was served as control group (NC). A water/cement ratio (w/c) of 0.44 (e.g. 592 g of cement and 261 g of deionized water) was practiced. Constant speed mixer was used to mix the nano materials with cement. API 10A standard was followed for the sample preparation. To do thus, the cement was mixed for 15 second under the rotational speed of 4000 r/min followed by the rotational speed of 12000 r/min for 35 sec. Attempts were made to add only 0.05 wt% nano glass flakes (NGFs) and multi walled carbon nano tubes (MWCNTs) to the cement and keep the cost of the design low.

Two different mixing approaches were considered: conventional/hand-mixing (H) and sonication (S). For the conventional mixing method, dry nano material powder was directly mixed into the cement and stirred for 5 min. For the sonication method, they were added into deionized water and sonicated at the room temperature by using 500W Probe Ultrasonic Processor. A frequency of 20 kHz and amplitude of 50% were applied on the suspensions. The sonicator was operated for 15 min to avoid overheating as suggested in the study of Konsta-Gdoutos et al [9]. All specimens were cured in a water bath for 24 hours under the temperature of 50°C and a series of thermal gravimetric, rheological and compressive strength tests were conducted. Table 1 reports the mixing proportion of the samples.



Figure 1. Physical appearance of nano glass flakes (NGFs)



Figure 2. b) Physical appearance of multiple-walled carbon nano tubes (MWCNTs)

Table 1. Type of cement samples

Label	Sample	w/c ratio, %	Type of Nano material	Mixing Method
1	Neat Cement (NC)	0.44	None	-
2	0.05NGFs-S	0.44	Nano glass flakes	Sonication
3	0.05 NGFs-H	0.44	Nano glass flakes	Conventional
4	0.05 MWCNTs-S	0.44	Multiple-walled carbon nano tubes	Sonication
5	0.05 MWCNTs-H	0.44	Multiple-walled carbon nano tubes	Conventional

3. Experimental Analysis

Stability test

Before mixing with the cement, the stability of the solution was tested using Malvern Zetasizer ZS. The zeta potential values of the treated nanoparticles offer an indirect indication of the net charge on the surface of nanoparticles. As a matter of fact, by defining the surface charge of nanoparticles in the solvent, their physical state in the solutions can be assessed and their stability is obtained. The term “stability” is referred to the tendency of particles to aggregate in an aqueous media.

Rheological measurement

The rheology of the MWCNTs and NGFs based cements were then measured using Fann Model 35 Viscometer. To do this, the cement slurry was poured into the viscometer cup and the readings were taken at different speeds i.e. 3, 6, 100, 200 and 300 rpm. Ascending and descending sequences were recorded after every 10 sec. The strain rate versus strain stress plots were then used to determine the rheological parameters including the viscosity and yield stress (see Figure 3). Viscosity is one of the inherent fluid properties, defining the relationship between the flow rate (shear rate) and pressure gradient (shear stress) that create the movement of the fluid [8]. Yield point is defined as an indicator to determine the threshold for the shear stress, which must be applied in order to put the slurry into motion. These two rheological parameters are important to evaluate the pumpability of the slurry and frictional pressure loss during placement [10].

Compressive strength measurement

To obtain the destructive compressive strength of the cement samples, semi-automatic Uniaxial and Triaxial test system (UTM) was used. It is a compression machine with a semi-automatic configuration, which could measure the axial loading and the maximum uniaxial confining stress that the samples could sustain under atmospheric condition. After curing, the cylindrical specimens with a diameter of 2.54cm and height 2.54cm (see Figure 4) were placed into the machine and the hydraulic load with the rate of 18 MPa/Min was applied on them. The changes of the force per area were then recorded by a computer running customized Windows® software over time.

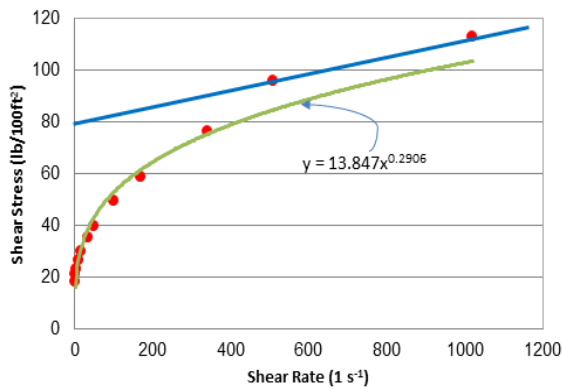


Figure 3. The analogy graph to obtain plastic viscosity and yield stress

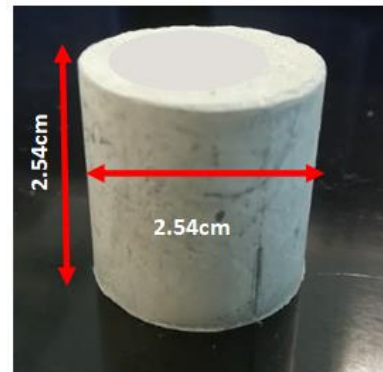


Figure 4. The cylindrical specimen used for UTM test

Stability of nanoparticles

The sensitivity of the solution to the variation of pH was also examined as part of this study with the results shown in Figure 5.

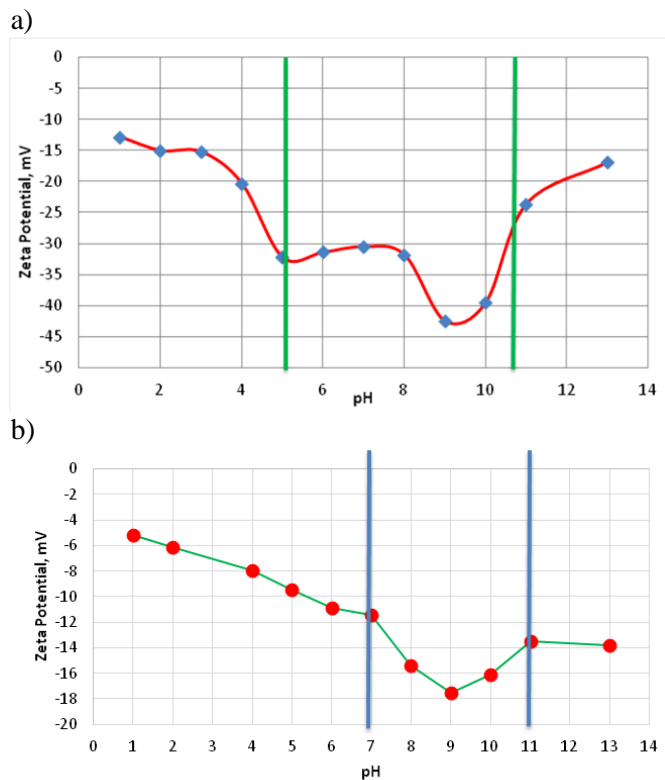


Figure 5. Zeta potential graph of a) NGFs and b) MWCNTs

As it is shown in Figure 5, NGFs and MWCNTs are negatively charged at the room temperature of 25°C. Both solutions have the highest negative charge at pH 9. As a matter of fact, NGFs reached -43 mV and maintained its negative surface charge of more than -30 mV within the pH from 5 to 11 whilst MWCNTs only achieved -18 mV the most. It was found that NGFs are comparatively more stable under an alkaline environment. Leonavičius et al [2] reported that a higher magnitude of zeta potential indicates a better stability to resist the aggregation of particles. This is mainly because at the lower magnitude (negative or positive), the attractive force between particles may overcome on the repulsive

force, resulting in aggregation and electrical instability. Hence, NGFs is possibly more stable compared to MWCNTs under any type of solutions.

4. Result and discussion

Rheology of nano based cement

The rheological models for nanoparticle-based cements and the results obtained are shown in Figure 6, Figure 7 and Table 2

As seen in Figure 7 and Table 2, 0.05 MWCNTs-S sample has the highest viscosity, 154.45 cP (increased ~10%) whereas NC has the lowest, 141.17 cP. The cements mixed with NGFs had very similar viscosities to those of the NC, within the range of 143 – 145 cP (~1.5% of increment), regardless of the mixing methods. Nevertheless, the sonicated (S) samples, in any case, demonstrated a higher viscosity compared to the conventional-mixed samples. This could be resulted from the water loss induced by the ultrasonic processor. It should be noted that the temperature of the solution increased from room temperature to ~60°C because of the mechanical vibration. This heat has led to water evaporation and accelerate the cement hydration, decrease the cement paste fluidity and eventually affect the viscosity [11, 12].

In general, NGFs based samples had a relatively lower viscosity. This could be resulted from a poorer integration between the cement and nanoparticles. In fact, NGFs particles are lighter than MWCNTs particles and they had a higher percentage of replacement once added to the cement by 5 wt% than MWCNTs. Thus, when the quantity is larger, without a proper dispersion, the particles are easier to be bounded together into macroscopic structures by Van der Waals forces, forming agglomerates [13]. Due to the presence of agglomerates, the molecules of the substances are unable to mix evenly, resulting in a higher mobility to flow.

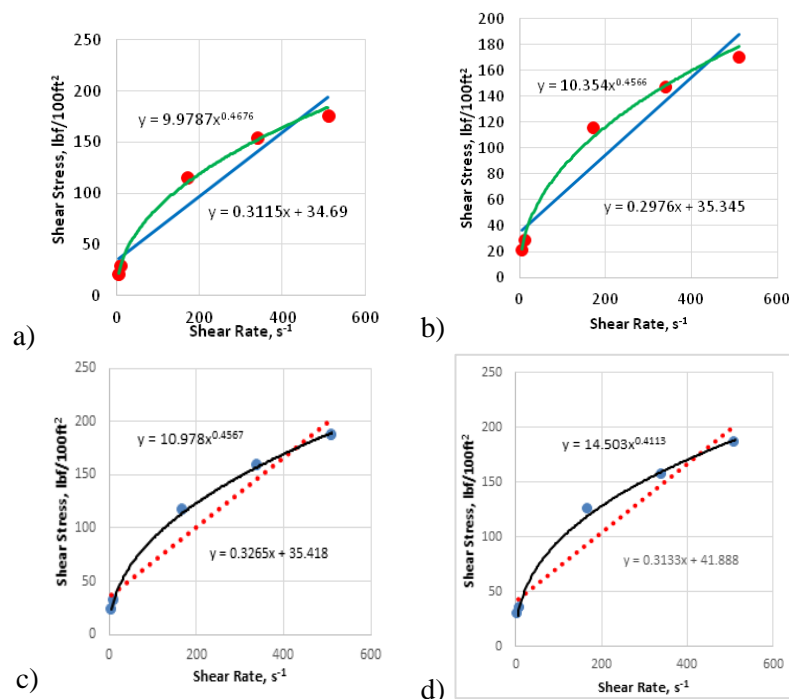


Figure 6. Rheological parameters and models obtained from a) 0.05NGFs-S; b) 0.05 NGFs-H; c) 0.05 MWCNTs-S; d) 0.05 MWCNTs-H

The yield stress or so-called yield point of the NGFs were very similar to the control sample (the neat cement), which are within the range of 34 lb/100ft²-36 lb/100ft². Although the highest viscosity

was acquired from 0.05 MWCNTs-S, the highest yield stress was gained from 0.05 MWCNTs-H. In spite of the types of nanoparticle used, hand mixed (H) samples had a greater yield stress compared to sonicated (S) samples. Poor particle distribution induced by the conventional mixing might be the reason behind this high yield point [14]. This indicates the fact that a good dispersion method must employed to ensure that the results obtained are consistent, reliable and trustworthy.

Table 2. Type of cement samples

Label	Sample	Viscosity, cP	Yield Point, lb/100ft ²
1	NC	141.17	34.978
2	0.05NGFs-S	145.27	34.69
3	0.05 NGFs-H	143.15	35.345
4	0.05 MWCNTs-S	154.45	36.22
5	0.05 MWCNTs-H	150.3	41.89

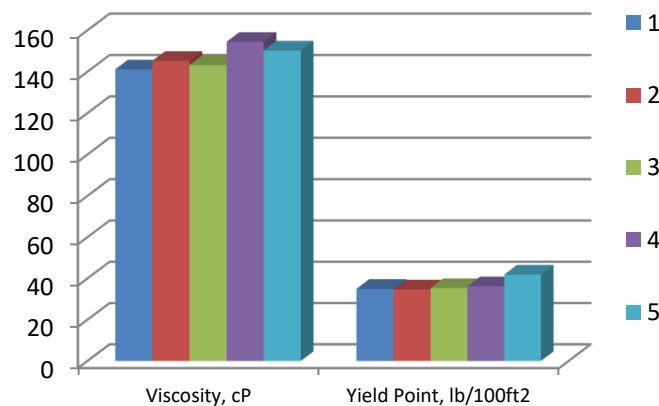


Figure 7. The rheological results of five specimens: viscosity and yield point/yield stress

Mechanical properties of nano based cements

The cement samples cured for 1 day were chosen for the compressive strength test. The strength was measured by the maximum force sustained before failure. The forces recorded at failure were divided by the cross-sectional area of the samples which was 0.000507 m². The results were then compared and tabulated in Table III and presented in Figure 8.

It was observed that 0.05 MWCNTs-S (label 1) samples had the highest compressive strength, ~28.41 MPa. The second highest compressive strength was obtained from 0.05 NGFs-S (label 2) samples, which was ~27.72 MPa. Conversely, 0.05 NGFs-H (label 3) sample had the lowest value, ~20.99 MPa, and it was followed by 0.05 MWCNTs-H sample with the strength of ~23.76 MPa. Both values were even lower than the strength of NC (~24.75 MPa).

Nevertheless, the conventional-mixing (H) samples had a relatively lower compressive strength than the sonicated (S) samples. The development rate of strength in the cement was negative with the hand mixed samples. This implies that even with a minimal replacement proportion, i.e. 0.05 wt%, a huge

difference is possible to be made if the nanoparticles are well dispersed. Cement hydration is essential for the compressive strength development. When 0.05 wt% of the cement is replaced by additives, the amount of Portlandite which is required for the cement hydration will be reduced. This reduction will affect the cement hydration rate if the additive does not disperse well in order to integrate with the cement particles. As a result, the compressive strength is decreased. Having said that, with the aid of a better dispersion, nanoparticles can be well distributed within the cement, without forming agglomerates. The large surface area of nano particles can increase the water absorption which favors the development of the cement hydration once the amount of Portlandite is decreased [15].

Table 3. The result of compressive strength for nano based cement

Label	Sample	Compressive Strength, MPa	Force, kN	Growth rate, %
1	NC	24.75	12.5	-
2	0.05NGFs-S	27.72	14	+ 12%
3	0.05 NGFs-H	20.99	10.6	- 15.19%
4	0.05 MWCNTs-S	28.41	14.4	+ 14.79%
5	0.05 MWCNTs-H	23.76	12	- 4%

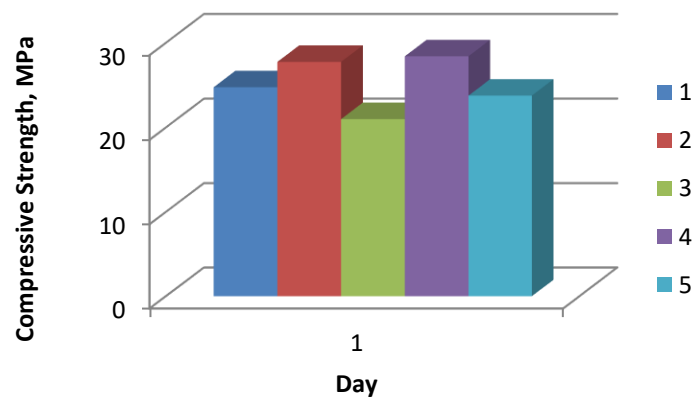


Figure 8. Compressive strength of nano based cement

5. Conclusion

The replacement of nano glass flakes (NGFs) and multi walled carbon nano tubes (MWCNTs) nanoparticles with the conventional Portland cement can improve the cement performance if a proper dispersion method is used. Sonication was found to be a good approach to reduce the agglomeration and improve the integration of the cement with the nanoparticles. Without a proper dispersion, even with a minimal replacement of nanoparticles, the cement performance will be negatively impacted. While improving the cement's mechanical properties, the presence of NGFs and MWCNTs in the cement did not significantly change the rheology. It was found that MWCNTs based sonicated cement can achieve

the highest compressive strength followed by 0.05 NGFs based sonicated cement. Since MWCNTs can endure an extremely high melting temperature, cement stability under different environmental conditions is expected. Technically speaking, MWCNTs appears to be a more attractive candidate to reinforce the oil well cement under an acidic HPHT reservoir condition.

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