DEVELOPMENT OF NEW NANO-PARTICLE-BASED WELL CEMENT FORMULATION FOR RESISTING POINT LOADS

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Abstract - Designing an appropriate cement slurry formulation for cementing wells in evaporite layers is a challenging task especially in deeper formations. Under HPHT (high pressure, high temperature) conditions, these layers are prone to creep toward the borehole which may consequently result in point loads on the cement sheath. Due to low flexural strengths of the conventional set cements, point loads are likely to cause cement failure and in some cases damage and collapse of casing string. A significant example of aforementioned problem occurs routinely in Gachsaran Formation (Miocene Age) in Southern Iran. In addition to concerns about low flexural strength of the cement, application of weighting agents are reported to cause severe inhomogeneity of the slurry due to high deposition of solid contents. Field and laboratory data confirm a rather high reduction of compressive as well as tensile strength of the cement caused by deposition especially in the lower parts of the well. In this study a systematic experiment design method was employed to obtain a cement slurry formulation to reduce cementing problems in Gachsaran Formation. Nano-Silica and Ex-RIPI which is a Single Walled Carbon Nano Tube (SWCNT) were utilized in formulation to improve rheological properties as well as tensile and compressive strength of set cement.The results of the experiments confirm that the application of Nano-Silica and SWCNT combined with an appropriate change in the percentage of other additives highly benefits the rheological and mechanical properties of the cement. Deposition of the solid contents is also shown to reduce significantly. Tensile and compressive strength of samples are improved. Other advantages are also obtained with these formulations, such as lower free water, lower setting time and lower fluid loss of the slurry.

Keywords - Cement, Fluid Loss, Nano-Silica, Strength, Drilling Well, Rheology, Slurry

I. INTRODUCTION

Strength assessment of concrete is a main and probably the most important mechanical property, which is usually measured after a standard curing time [124]. In recent years, the technology of nano-structured materials is developing at an astonishing speed and is being applied extensively into many materials and systems [101]. Studies have shown that the content and specific surface area of nano-particles have a strong influence on the water demand of cement paste [121, 122, 123]. Hui et al. have worked on cement mortars with nano-SiO2 and nano-Fe2O3 to explore their super mechanical potentials [102]. In another work, Senff et al. have studied the effect of nanosilica on the rheology and fresh properties of cement pastes and mortars [103]. In their work, rheological tests showed that after 75 min of starting the mixing, the mortar having 2.5wt% nanosilica shows insufficient flow ability to allow its continuous monitoring in a Viskomat PC viscometer. Moreover, with the nanosilica addition, spread, setting time and the moment to reach the maximum temperature decreased, compared with samples without nanosilica.

Even though nano scale materials can result in dramatically improved properties, there are few reports on mixing nano-structured materials in cement-based building materials. One of the most useful nano materials that have received considerable attention in many fields especially in well cements is nano-silica [101]. In the petroleum industry, cements are used in well operations. In these operations, cement is typically utilized to fill the annular space between the pipe and rock formation, displace the drilling fluid, support the casing and protect it against corrosion and impact loading, restrict the movement of fluids between formations, and isolate productive and non productive zones. Well cements are used in different conditions of exposure than cements used in the conventional construction industry. They are employed within large temperature ranges from below 0 ◦C in permafrost to 100 ◦C in some secondary recovery operations. The strength of well cements always depends on some deferent factors such as time and conditions of curing [104,105], environmental conditions [106,107], slurry design and use of additives [108,109], and also any additional treatments to which the hardened cement blends are subjected [110, 111].

Nano-SiO2 can react with calcium hydroxide (Ca(OH)2) crystals, which are arrayed in the interfacial transition zone (ITZ) between hardened cement paste and aggregates, and produce C–S–H gel. Thus, the size and amount of calcium hydroxide crystals are significantly decreased, and the early age strength of the hardened cement paste is increased [113, 114]. Carbon nanotubes (CNTs) have an ideal structure formed by carbon atoms with one dimension [116]. They are seamless tubes of graphite sheets with nano-sized diameter [117]. Having the best performance among carbon materials, it is expected that carbon nanotubes can remarkably enhance the performance of cement composites [117]. Lots of

researches showed that treated carbon nanotubes can enhance the reinforcement efficiency of the set cement [118, 119, 120]. Indeed, the results show that the addition of carbon nanotubes to cement can improve both its mechanical behavior and microstructure. For comparison, the effect of both nano-SiO2 and SWCNTs on rheological properties of cement slurry and mechanical properties of set cement were studied.

II. MATERIALS AND PROCEDURES

The most commonly used wellbore cements are the Classes A, G and H, Portland-based cements [115]. The cement powder used was Tehran class E ordinary portland cement (OPC) according to the (API) standards, and the colloidal solution of spherical nano-SiO2 (nano-SiO_2) particles which were synthesized in Iran. About 40% by volume of this solution is nano-SiO2 particles. The particle size of this additive is about 20-30 nm and the specific area of it is about 250m^2/gr. The other nano material used in study is Ex-RIPI which is provided by the Nanotechnology Department of RIPI. At least 60% by volume of this powder like additive is SWCNT. These nanoparticles' diameters are around 25 nm and in order to fully dispersion, they had been chemically surface treated. Other additives such as dispersants, antifoam agent, weighting additives and fluid loss control were used in the admixture of cement slurry. For all cement slurry formulations, just fresh water have been used.

The sample preparations were done in accordance with API RP 10B-2, 2005 [125]. The specification gives the standard procedure for sample conditioning prior to testing. For the initial mixing, a high speed propeller-type mixer is used. The additives were added to the water successively in the mixer with the mixing intervals of 20 sec at 4000 rpm. First, for the NET specimen salt has been added to the fresh water in order to make saturated salty water. Then fluid loss controller and retarder have been added and finally weighting additives and cement powder premixed and thereafter have been added to the solution. They blend for 2 min at the speed of 4000 rpm in the mixer and 35s at the speed of 12000 rpm. In order to add a certain amount of colloidal nano-SiO_2 solution into the cement slurry, we reduced the same volume of fresh water and after mixing with salt, we added that volume of colloidal nano-SiO_2 solution to the salty water. So, the total volume of solution remained fixed. Also, in order to design a slurry formulation by use of Ex-RIPI, we just substitute a certain grams of a weighting agent with it. Table 1 illustrates the compositions of all the cement slurry formulations investigated in this study those all have 153 pcf weight. Rheological properties such as YP and PV, Free-water, fluid loss, thickening time and mechanical properties such as compressive strength and tensile strength, calculation of Yaung's modulus, Poison's ratio and plotting the stress-strain curves are the tests have been performed for each formulation.

Cement Slurry Formulations

Slurry weight: 153 pcf, Bottom Hole Circulating Temperature =93°C , Bottom Hole Static Temperature=110°C

No.	Formula Name	Cement Class E Tehran (gr)	Hidense (gr)	Micromax (gr)	Salt (gr)	CFL-325 (gr)	Boric Acid (gr)	Nano-SiO_2 (cc)	EX-RIPI (gr)	Water (cc)
1	NET	1000	635	164	157	14	3.3	-	-	460
2	NS-1	1000	635	164	157	14	0.8	82	-	381
3	NS-2	1000	635	164	157	14	1	165	-	300
4	ExRIPI 1	1000	635	159	157	12	3	-	5	460
5	ExRIPI-2	1000	635	154	157	12	2	-	10	460

Table 1: Composition of slurries in this study

Rheology

The rheological properties are a very important indicator of the stability of the slurry as well as determining the appropriate fluid regime to optimize mud removal [126, 127], calculate the pressures and the relevant equivalent circulation densities (ECDs). To avoid the generation of channels on the high side of the pipe and the uniform placement of cement slurry across the entire open-hole section, the slurry needed to possess low fluid loss control with zero free water and segregation development [128].

At first, the cement slurry was poured into a slurry container for the preconditioning process. After applying the desired conditions the slurry was stirred for about 20 min, and then it was immediately poured in to a viscometer cup. During the tests the viscometer cup, bob, and sleeve were kept at the test temperature using a heated cup assembly. Throughout this time the slurry was stirred in order to prevent it from remaining static. The temperature of the slurry was recorded before the first reading, and the first reading was taken 10 sec after continuous rotation at the lowest rotating speed. After that, the remaining readings were taken first in ascending order, and then in descending order following continuous rotation of 10 sec at each speed. After reading each speed, in order to continue the reading process, the speed was immediately shifted to the next considered speed. At the end, the temperature of the slurry in the viscometer cup was recorded again. The rheological measurements were reported as the average of (ramp-up + ramp-down)/2, at the average temperature of the slurry in the viscometer cup in the beginning and the end of the process. These tests were done according to API RP 10B-2, 2005 [125] using the Fann 35 viscometer.

Free-Water test

The cement slurry is indispensably in a liquid state for a period of time down-hole and it can lead to increased solids segregation and free water generation. Free water generation by cement slurries in horizontal sections of oil and gas wells is more disadvantageous to the overall annular isolation than

the vertical sections. In order to verify free-water content an atmospheric pressure consistometer or pressurized consistometer is used for stirring the cement slurry. After measuring the rheological properties at BHST, the slurry was used to measure the free-fluid test. So, the cement slurry stirred in an atmospheric consistometer for 20 min±30 sec at a speed of 150±15 rpm (2.5±0.025 r/sec), and a temperature of 93±1.7 ◦C. Then, After 2 hr being in completely static condition, the volume of developed supernatant fluid was measured by an accuracy of ±0.1 ml and it was recorded as milliliters free water (Fig. 1). Later the milliliters free fluid will converted to a percentage of the started slurry volume representing the value as percent free fluid, utilizing the following formula:

$$\%FF = \frac{V_{FF} \cdot \rho}{ms}.100$$

%FF is the free content of the slurry in percent; VFF is the volume of free fluid (supernatant fluid) collected (ml). ρ is the specific gravity of the slurry (g/cm^3) and mS is the initially recorded (starting) mass of slurry (g).

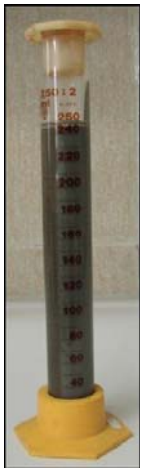


Figure 1: free water test for a vertical well

Fluid Loss Control

This test, evaluate the capability of cement slurry to maintain its water phase and prevent it to loss into adjacent formations. Loss of mix water from the slurry, during displacement, will reduce the slurry's thickening time and increase its viscosity. As the slurry loses water it will lay down a filter cake, against the permeable formation wall. Uncontrolled, this will change the flow regime of the slurry from the calculated one to some unpredictable alternative and may result in excessive ECD being experienced during displacement. To reduce the amount of fluid lost from the slurry to the permeable reservoir section, slurries must have an API fluid loss of less than 80mls in 30min, tested with a differential pressure of 1000psi and at bottom hole static temperature.

Thickening time

The apparatus for measuring thickening-time consists of a pressurized consistometer consisting of a rotating cylindrical slurry container, equipped with a stationary paddle assembly. At first the slurry was loaded in to a slurry container and it was placed in a pressure vessel, the temperature and pressure of the cement slurry were increased according to the appropriate specification schedule [125]. The thickening time was recorded as the passed time between the first application of temperature and pressure to the pressurized consistometer and the time at which a consistency of 100Bc was reached (Bearden unit of consistency (Bc) is the measure of the consistency of a cement slurry). Finely, the maximum consistency between 15 min and 30 min of the stirring period was reported [101].

Compressive Strength

Compressive strength is the capacity of a material or structure to withstand axially directed pushing forces. It provides data of force vs. deformation for the conditions of the test method. The splitting tests are well known indirect tests used for determining the tensile strength of set cement or concrete. The test consists of applying a compressive line load along the opposite generators of a concrete cylinder placed with its axis horizontal between the compressive platens. Due to the compression loading a moderately uniform tensile stress is developed over nearly 2/3 of the loaded diameter as obtained from an elastic analysis.

To investigate the strengths parameters of set cement, two cylindrical molds with standard dimensions have been cured in curing chamber for 48 hr at 110 ℃ and 3000 psi. One for measuring the axial compressive strength, Young modulus, poison's ratio and also to plot the stress-strain diagrams and the other one have been cut down into three or four disks in order to perform splitting tensile strength test (ASTM-C496 test) which called Brazilian test in rock mechanic. The average amount of Young modulus, Poison's ratio and maximum axial compressive strength for all formulations have been shown in table 2. Table 3 illustrates the average of splitting tensile strength of all formulations after 48 hr curing.

No.	Formula Name	Peak Load (psi)	Poison's Ratio	Young Modulus (GPa)
1	NET	2346	0.34	6
2	NS-1	2974	0.52	8
3	NS-2	3045	0.7	6
4	EXRIPI-1	1911	0.21	12.2
5	EXRIPI-2	1580	0.74	4.9

Table 2: the amount of Young modulus, Poison's ratio and maximum axial compressive strength

No.	Formula name	Average Failure Load (KN)	Average Tensile Strength		Condition
			(Psi)	(MPa)	
1	Net	8.33	333.6	2.30	Saturated
2	NS-1	10.5	382.9	2.64	Saturated
3	NS-2	10.66	432.2	2.98	Saturated
4	ExRIPI-1	10.33	397.4	2.74	Saturated
5	ExRIPI-2	11.677	440.9	3.04	Saturated

Table 3: characteristics of specimens and the results of splitting tensile strength test on them

III. RESULTS AND DISCUSSION

Rheological Properties

All the experimented slurries containing nano-silica showed thixotropic behaviors; also by the use of dispersants, they showed a low consistency. The rheological properties of all cement slurries, which showed an acceptable compressive and tensile strength, can be seen in Table 4. After adding nano particles into cement slurry formulas, The amount of YP and PV have been modified by making changes in other additives like dispersant or retarders and etc. So, especially all cement slurries YPs are in the desired rang in order to be in best rheological condition to be used in field projects.

No.	Formula name	Heat Condition	PV	YP	Fluid loss (cc)	API Free Water (cc)	Mixing Time (sec)
1	NET	Before Heat	109	1	29	36	20
		After Heat	28.5	-0.5			
2	NS-1	Before Heat	177	1.5	25	29	32
		After Heat	51	2			
3	NS-2	Before Heat	244	3	20	26	45
		After Heat	81	2			
4	ExRIPI-1	Before Heat	118	1	42	30	43
		After Heat	117.5	0.5			
5	ExRIPI-2	Before Heat	115	1	40	33	40
		After Heat	106	1			

Table 4: Rheological properties of all cement slurries formulas

Free-Water and Fluid loss

The amount of free water and fluid loss of the cement slurry was measured according to the API RP 10B-2, 2005 in order to show the stability of slurries [125]. The results demonstrate considerable decrease in both free water and fluid loss in the designed slurries using nanosilica (Fig. 2).

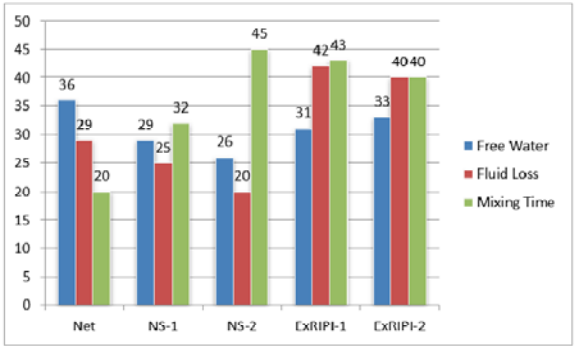


Figure 2: results of free water and fluid loss and mixing time tests

It caused 28% decrease in free water and 31% decrease in fluid loss. Using SWCNT caused a little decrease in free water (nearly 8%) but there are considerable increases in fluid loss approximately 17%. So, in this case adding SWCNT to the cement slurry formulation hadn't significant effect on cement slurry free water, however it dramatically increased fluid loss. In comparison with nano-SiO_2, Ex-RIPI which contains SWCNT has much less effect on the C-S-H gel.

Mixing Time

Mixing time is another parameter which should be in a rational range about less than 50 to 60 sec for drilling cement slurry in order to be useable in field projects. High amount of this Item can cause failure in mixing operation in field. In this case, mixing times are in rational range for all formulations. Using nano-SiO2 caused considerable increases of mixing times which have been shown in figure 2. The amount of nano-SiO_2 in slurry named NS-2 was the highest amount of nano-SiO2 that could be used and using more than this amount caused high mixing time, being so viscous and also high amount of YP without any solution to decrease it eve by other additives such as dispersant. In contrast, using SWCNT caused high mixing time for both quantities of SWCNTs used in formulas. It showed that the SWCNT is naturally hard to mix partly due to their high hydrophobicity and partly due to their strong self-attraction [129,130].

Compressive Strengths

Both compressive and tensile tests are carried out according to ASTM. Figure 3, 4 and 5 show the axial and diametric stress-strain curve of three of the cement slurry formulations. In the left part of these figures there are axial stress- diametric strain curves and in the right part there are axial stress-axial strain curves. The ratio of the slope of the curves in the right called Young's Modulus to the slope of the left one represents Poison's Ratio. Te less Young's modulus and the more Poison's ratio is the final aim.

Figure 6 shows peak load of all set cement formulations. It can be seen that adding and increasing nono-SiO2 into cement slurry formulation redound to axial compressive strengths of set cements and improved it about 30%. But in contrast, adding and increasing the amount of SWCNT into cement slurry formulations caused highly decreases of axial compressive strengths more than 31%. Figure 7 show Young modulus and Poison's ratio of all set cement formulations. There are just a few changes in Young's modulus when nano-SiO2 had been used but this additive highly affected Poisons ratio and increase it over 200%. In other hand, SWCNT caused approximately 18% diminish in Young's modulus. SWCNTs strongly improved Poison's ratio and nearly 217% increased it.

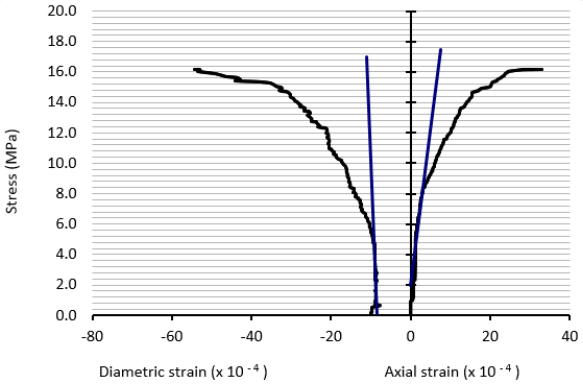


Figure 3: axial and diametric stress-strain curve of NET cement slurry formula

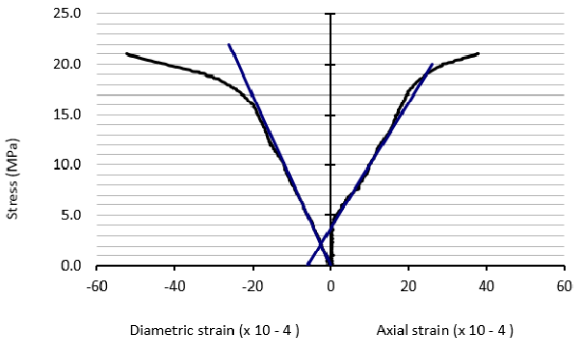


Figure 4: axial and diametric stress-strain curve of NS-2 cement slurry formula

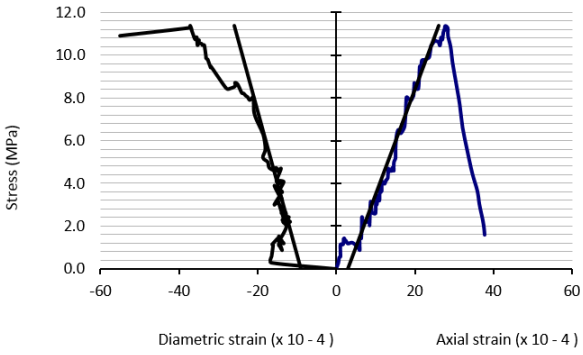


Figure 5: axial and diametric stress-strain curve of ExRIPI-2 cement slurry formula

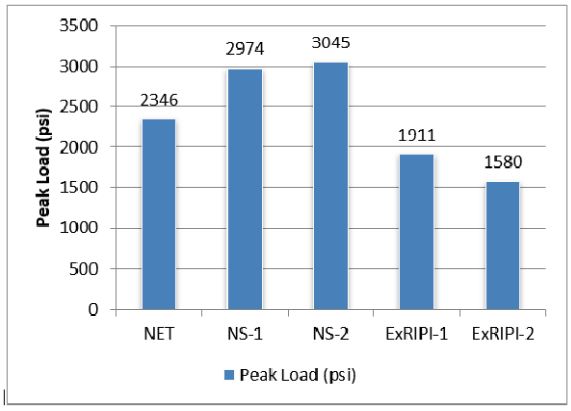


Figure 6: peak load of all set cement formulations

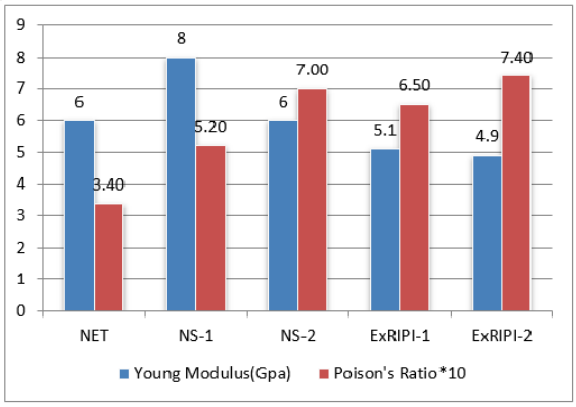


Figure 7: Young modulus and Poison's ratio of all set cement formulations

IV. CONCLUSION

The mechanical and rheological properties and microstructure of the cement composites containing nano-SiO_2 and SWCNTs have been investigated through experimental study. The SWCNTs used were chemically surface-treated.

Based on the results, adding nano-SiO_2 to the cement slurry formulation highly improved rheological properties of cement slurries. It caused highly decreasing of fluid loss and free water and also prevent from settlement of solid contents. Also, compressive strength tests and SEM images showed that nano-SiO2 behaves not only as a promoter of hydration reactions but also as a filler to improve set cement microstructure and decreases the porosity of cement composites. Therefore, the newly formulated cement composites become much more compacted and uniformed. Also, results revealed that nano-SiO_2 can efficiently improve splitting tensile strength and Poison's ratio as well.

On the other hand, Using SWCNT led partial improvement of rheological properties of cement slurry compared to nano-SiO_2. It caused reduction of free water but in this case SWCNT was unable to decrease the fluid loss. It might be just because of the effect of SWCNTs on the filter cake of cement slurry. Interfacial interactions between surface treated SWCNTs and hydrations (such as C–S–H gel) of cement slurry will produce a high bonding strength led to improvement of the material microstructure and the bridge coupling effect which consequently lead to load-transfer efficiency of set cement. Moreover, SWCNTs acts as filler and it will fine pore size distribution and decreases the porosity of cement composites. Basically, it's visible that nano-SiO_2 has more effect on rheological and compressive strength of the cement formulas than SWCNTs. Although nano-SiO_2 greatly improved tensile strength and poison's ratio, but these improvements are in accordance with Ref. [112] which indicated that high-strength concrete with nano-SiO2 has higher flexural

strength. But SWCNT directly affect and improved tensile strength and Poison's ratio even more than nano-SiO2. Further study in this direction is recommended.

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