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Tensile Strength of Oil-Well Cement Pastes Produced with Carbon Nanotubes Directly Synthesized on Clinker

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---**ABSTRACT**---
This paper analyzes the influence of carbon nanotubes (CNTs) in the tensile strength of cement slurries used in oil wells. CNTs were directly synthesized on cement clinker by chemical vapor deposition process. Cement slurries containing 0.1% and 0.3% of CNTs bwoc were compared with CNT-free slurries. Polynaphtalene sulfonated (0.2% bwoc) was used as dispersant in all cement slurries. Tensile strength was evaluated at the age of 28 days. The results show the presence of CNTs in the cement slurries increases the tensile strength in approximately 65% for 0.1% CNT bwoc at age of 28 days.
***KEYWORDS** - carbon nanotubes, cement paste, tensile strength, oil wells.*

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I. INTRODUCTION

Well cementing is one of the most important operations performed in oil or gas wells. During cementing procedures, a suspension consisting in water, cement and performance controlling chemicals is pumped down into the well and placed at the interval between the case and the rock formation and left to cure. The purpose of this operation is to anchor the casing to the formation and to achieve the zonal isolation down in the well. The anchoring of the casing is usually achieved but the challenger is to obtain a complete zonal isolation [1].

Discoveries of new reserves in adverse conditions of exploration and the need to recover mature wells may create severe temperature and pressure conditions during cementing procedures. Therefore, flaws in well cementing have increased and required a greater number of interventions during production. They increase production costs and may affect the environment [2, 3].

The high temperature and pressure within an oil well often requires a particularly resilient cement system and the use of a number of high tech chemical admixtures to help ensure adequate zonal isolation [4]. With regard to the desired mechanical properties in oil wells cements, the Young's modulus should be a low is possible, while the tensile strength of cement should be as high is possible. Conventional Portland cement slurries have a tensile- to - compressive strength ratio of approximately 10%. If this ratio were to be increase as high is possible, the life of cement sheath in a given well would been extended. Mechanical property enhancements would not be complete without tensile strength gain. This is the one of reasons for the investigation of carbon nanotubes (CNTs) cement composites. CNTs have been reported to yield a significant enhancement of tensile properties in cements [5].

Carbon nanotubes are graphene sheets rolled up to form cylinders tubes. A single walled CNT looks like a single sheet rolled up into a tube, while multiwall CNTS look like multiple sheets rolled in to a series of tube, one inside the order [6].

According to [5], CNTs behave as one-dimensional material. In addition, they present tensile strength and Young's modulus values ten times greater than steel and a density five times smaller [7, 8, 3]. Consequently, CNTs have very high aspect ratios (length/diameter ratio) and can be distributed widely and densely at the microscopic scale yet covering longer lengths.

These characteristics can be used in cement composites to bridge cracks and restrict them from increasing which can essentially create a new generation of crack-free materials [6, 8, 9, 10, 3].

Carbon nanotubes used in this investigation were synthesized directly onto the grinded clinker in order to create a low cost cementitious nanostructured material. Converter dust was employed as iron precursor in the chemical vapor deposition (CVD) process. The use of these materials and procedures allows large-scale production of a nanostructured cement at a reduced cost [11]. In the CVD process, the carbon source is deposited on a catalyst, which causes it to decompose into carbon atoms and consequently create tubular CNTs with diameters equivalent to the catalyst particle size. CVD has the advantages of mild operations conditions, low costs, and controllable synthesis. Thus is the most promising method for CNT production at industrial scale [12]. Based on this scenario, the objective of this investigation is to analyze the tensile strength of oil-well cement slurries produced with clinker manufactured with carbon nanotubes.

II. MATERIALS

In this study, multiwall carbon nanotubes were synthesized directly onto the grinded cement clinker in the Laboratory of Nano-materials of the Federal University of Minas Gerais, Belo Horizonte, Brazil [11]. Converter dust was employed as iron precursor in the chemical vapor deposition (CVD) process. This way, the produced CNTs have a natural functionality due to the defects they present in their shapes and outer walls. Maximum CNTs length was in the order of tens of microns. Mean diameter of CNTs was between 50 and 80 nm. Thus, the average CNTs aspect ratio was approximately 1000.

Figure 1 shows scanning electron microscopy (SEM) images of the CNTs grown directly onto the cement clinker. It can be seen that CNTs are well distributed on the clinker particles and have polydispersity of length and diameter.

The nanostructured clinker contained 9% of carbon nanotubes by weight, as determined by a thermogravimetric analysis (Figure 2). It can be observed that nanostructured clinker thermogravimetric analysis showed two peaks with significant mass loss for the same temperature range. According [13], the two mass loss peaks correspond to the two main types of carbon nanotubes grown onto the clinker.

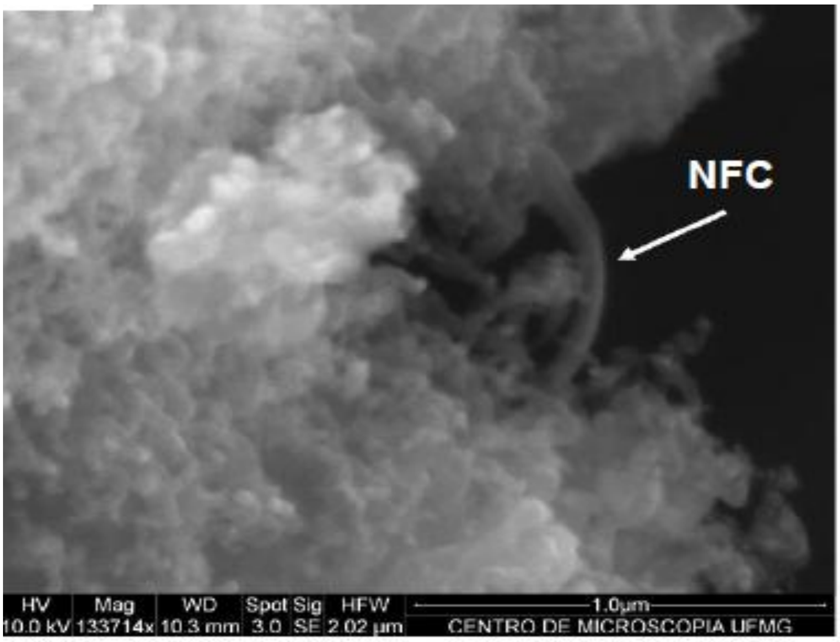

Figure 1: SEM images of CNT/CNFs grown directly onto the cement clinker.

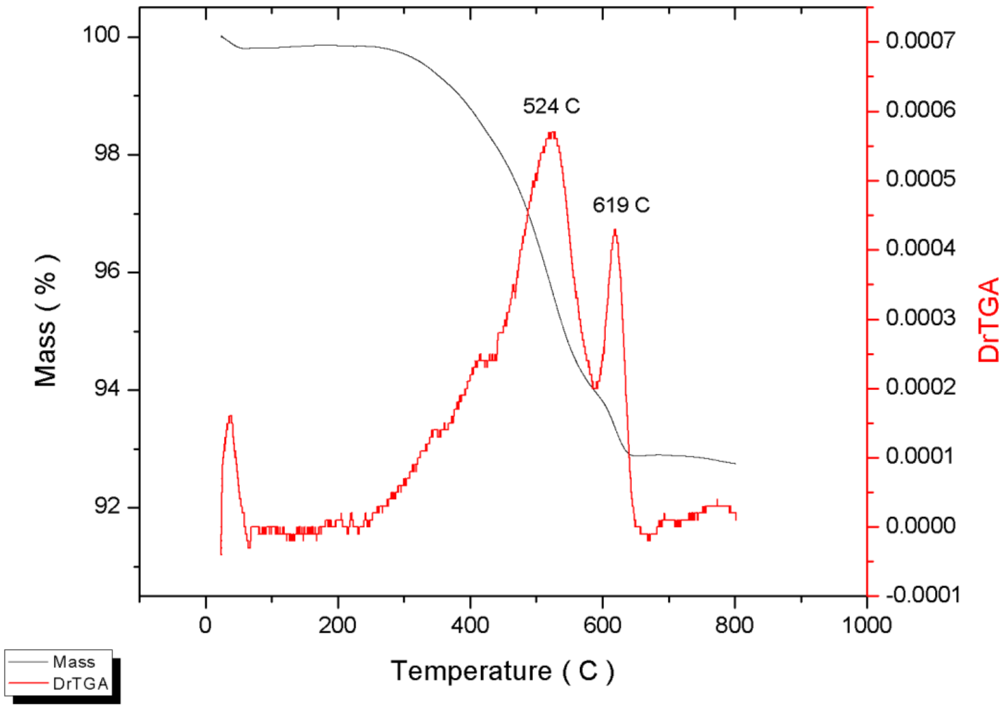

Figure 2: Thermogravimetric analysis of nanostructured clinker.

It is important to emphasize that in this carbon nanotube (CNTs) growth process there is no need for chemical functionalization [11]. The used catalysts are residual materials of the mining and steel industry. Thus, it is undoubtedly a much simpler, cheaper and lesser time consuming way to produce functionalized CNTs to be used in cement composites. It also allows for large-scale production, which can be employed during the cement manufacture.

Surfactants were used for the dispersion of clinker containing CNTs in cement slurries. In this particular case, a polynaphthalene sulfonated based dispersant was employed. Table 1 presents the materials used in cement slurries with and without carbon nanotubes. Tables 2 and 3 show chemical and physical characteristics of the Brazilian API Type G Portland cement used in these studies. These results were obtained from tests performed at Petrobras Research Center (CENPES) in Rio de Janeiro.

Table1: Materials used in composition of the oil-well cement slurries.

Class	**Material**
Cement (Holcim)	Brazilian APE Type G Portland Cement
Carbon nanotubes (CNTs)	CNT grown direct onto cement clinker
Surfactants (Halliburton)	Polynaphtalene sulfonated
Water	Distilled water

Table2: Chemical characterization of Brazilian API Type G Portland Cement (Holcim ™)

Chemical characterization	**Standard requirements (Brazilian NBR-9831) (%)**	**Sample (%)**
Loss on ignition	≤ 3.00	0.71
MgO	≤ 6.00	2.21
SO_3	≤ 3.00	2.22
Insoluble residue	≤ 0.75	0.13
Free CaO	≤ 2.00	0.74
Total alkali content (NaO equivalent)	≤ 0.75	0.57
C_3S	48 - 65	60.80
C_3A	≤ 3.00	2.16
$2C_3A+C_4AF$	≤ 24.00	19.55

Table 3: Physical characterization of Brazilian API Type G Cement (Holcim)

Physical characterization	**Standard requirements (Brazilian NBR-9831)**	**Sample**
Specific gravity		3.19 g/cm^3 (26.63 lb/gal)
Setting time at 52ºC (125ºF)	90 - 120 min	112 min
Compressive strength, 8 h at 38ºC	≥ 2.1 MPa	3.93 MPa
Compressive strength 8 h at 60ºC	≥ 10.3 MPa	13.39 MPa

III. METHODS

Oil well cement slurries were made according to [14] to ensure a constant specific mass of 1.9 g/cm3 (15.8 lb/gal) and a water/cement (w/c) ratio of 0.44. The total cement content was equal to 1313 kg/m3 (81.97 lb/ft2) in all cases. A polynaphtalene sulfonated based plasticizer was employed to enhance the workability of the fresh cement and dispersed CNTs. The plasticizer/cement ratio was 0.2%. The content of CNTs was 0.1% and 0.3% of binder weight (cement and clinker containing CNTs). These amounts of CNTs were based on results obtained by [15, 11].

In order to studied the CNT aspect ratio importance in mechanical strength, clinker containing carbon nanotubes was ground in a ball mill for 5, 10 and 15 minutes. Evaluation of scanning electronic microscopy (SEM) images showed that CNTs shredded for 10 minutes had lower average lengths and, consequently, lower aspect ratios. Thus, a 10-minute grinding time was chosen.

Five different pastes were mixed and tested. Table 4 shows the composition of each one and the corresponding denomination, which will be referred to in this paper.

Table 4: Cement pastes compositions.

Cement paste Denomination	**Composition**
PNS02	Cement + water + 0.2% PNS*
PNS02CNT01	Cement + water + 0.2% PNS + 0.1% CNT (bwoc)
PNS02CNT01p	Cement + water + 0.2% PNS + 0.1% short length CNT (bwoc)
PNS02CNT03	Cement + water + 0.2% PNS + 0.3% CNT (bwoc)
PNS02CNT03p	Cement + water + 0.2% PNS + 0.3% short length CNT (bwoc)

*Polynaphtalene sulfonate based dispersant (Halliburton TM).

The cement paste preparation followed the procedures prescribed by [14]. In this case of pastes with carbon nanotubes, the necessary amount of clinker containing CNTs was first mixed with Brazilian API Type G Portland cement in plastic bag for 2 minutes. This procedure was used to disperse and homogenize the CNTs into the cement. For each cement slurry batch, four 25.4 × 50.8 mm (1×2 in) cylinder specimens were cast. They were cured in water at 27ºC until the time of testing which corresponded to 28 days. The specimens were removed from the water bath and wiped dry with a paper towel just before testing; this procedure was used to ensure that the specimens maintained approximately the same moisture content.

The tensile strength was measured by splitting tensile test (Brazilian tensile test). Four specimens were used at each testing date. Tests were performed at a constant displacement control rate of 0.5 mm/min (Fig. 3).

Figure 3: Splitting tensile test.

IV. RESULTS AND DISCUSSIONS

Table 5 presents the results of the splitting tensile strength of cement pastes at 28 days.

Table 5: Cement pastes splitting tensile strength at 28 days

Cement Pastes	**Splitting tensile strength – 28 days (MPa)**
PNS02	3.55 ± 0.14
PNS02CNT01	5.86 ± 0.19
PNS02CNT01p	5.55 ± 0.57
PNS02CNT03	5.13 ± 0.57
PNS02CNT03p	5.50 ± 0.59

The tensile strengths at 28 days of 0.1 and 0.3% (normal or short length) CNTs cements pastes are higher than CNT-free paste. The paste with 0.1% normal length CNTs showed a 65% increase in the splitting tensile strength with respect to CNT free slurries. This finding suggests that carbon nanotubes may act as nucleation points for the hydration products of the cement.

V.CONCLUSIONS

In this investigation, carbon nanotubes (CNTs) were synthesized directly onto cement clinker by chemical vapor deposition (CVD) process. Converter dust was employed as iron precursor in the CVD procedure. This way, the produced CNTs have a natural functionality due to the defects they present in their shapes and outer walls.

The tensile strengths at 28 days of 0.1 and 0.3% (normal or short length) CNTs cements pastes are higher than CNT-free paste. The paste with 0.1% normal length CNTs showed a 65% increase in the splitting tensile strength with respect to CNT free slurries. This finding suggests that carbon nanotubes may act as nucleation points for the hydration products of the cement.

With respect to CNT content in cement slurries, the results herein suggest better performance at the 0.1% CNT bwoc.

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