Cement Sheath Modification Using Nanomaterials for Long-term Zonal Isolation of Oil Wells: Review

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Abstract

Well cementing is an important operation during drilling and completion of oil wells. The cement sheath must maintain well integrity behind the casing and provide long-term zonal isolation to ensure safety and prevent environmental problems. Despite recent technological advancement in smart polymeric materials, fibers and self-healing materials, it is still a big challenge to provide adequate long-term zonal isolation in severe oil well conditions. This review provides an overview of challenges faced in oil wells compromising the long-term ability of the cement sheath to provide zonal isolation. Factors controlling the long-term performance of cement sheath are discussed, in terms of shrinkage, tensile strength and flexibility. The use of nanomaterials as cement additive to fabricate flexible, high-tensile strength, and low-shrinkage cement system are reviewed. Introduction of nanomaterials into the cement system is a promising approach to design a sealant for the entire life of the well, thereby avoiding potential remedial costs and environmental impacts.

Keywords: Oil well cement; Shrinkage; Tensile Properties; Young's modulus; Nanomaterials

1   Introduction

Nanotechnology applications have pierced through oil industry in the four general petroleum disciplines: exploration, drilling, production and reservoir. The possibility to produce tailor-made nanomaterials with specific properties is expected to play a leading role in dealing with challenges encountered in different areas of the oil industry (Li et al., 2013). For example, nanoparticles may provide sophisticated measuring and imaging tools to improve field characterization techniques in oil exploration (Krishnamoorti, 2006; Pourafshary et al., 2009). Nanosensors compatible with hostile environments in deep wells are being developed for reservoir management (Zhang et al., 2011). Also, there has been a great focus on Enhanced Oil Recovery (EOR) using nanotechnology.

Application of nanoparticles such as oxide nanoparticles, polymeric nanoparticles and nanoemulsions have demonstrated improved and cost-effective EOR processes (Del Gaudio et al., 2007; Morales et al., 2003; Zargartalebi et al., 2015). Nanotechnology has also led to the introduction of a new generation of smart fluids for drilling and completion applications. These smart fluids contain nanoparticles and provide advantages like wettability alteration, advanced drag reduction and sand consolidation, enhancing the drilling process (Matteo et al., 2012). Among others, nanopalygorskite has been found to deliver stable drilling fluid providing excellent penetration rates, enhanced lubricity, and improved wellbore stability at high temperature high pressure (HTHP) environments (Abdo and Haneef, 2013).

Nanotechnology is being increasingly introduced to improve the well cementing process. Conventional cement-based materials are naturally brittle, display low tensile strength and bulk shrinkage. These features result in poor performance in bottomhole condition and finally, costly repair operations, reduction in production capacity, environmental issues, and in worst case loss of the well (Jimenez et al., 2016). Application of nanotechnology in well cementing is a promising approach to convert conventional cement system into multifunctional, durable system to deal with imposed stressful conditions for entire life of the well. From cement sheath perspective, as hydrocarbon resources are becoming gradually depleted in easy-to-recover environments, hostile downhole conditions are more common (Jimenez et al., 2016). Additionally, thermal and stress cycles created by well events such as hydraulic fracturing, production, completion, steam injection, or remedial treatments during the well's life, poses significant challenges to the cement sheath integrity (Shadravan et al., 2014). Therefore, taking new approaches are required to design a cement system to withstand the potential severe conditions during well's life cycle. In order to enhance cementing process, nanospacer based on nanoemulsion technology has been introduced as a new method for enhancing mud displacement efficiency, resulting in better mud removal, wettability change and better casing/formation adhesion of the cement sheath (Maserati et al., 2010). In addition, nanomaterials have been applied in the oil well cementing industry to accelerate the cement hydration (Pang et al., 2014), improve the mechanical properties of the cement sheath (Mercado et al., 2012; Roddy et al., 2010; Roddy et al., 2013), control fluid loss, reduce the probability of casing collapse, and prevent gas migration (Roddy et al., 2013). In summary, nanotechnology has been applied by the oil well cementing industry to solve problems which cannot be solved by conventional approaches.

There are several reviews of nanotechnology application in construction materials, e.g. (Andersen and Geiker, 2009; Hanus and Harris, 2013; Pacheco-Torgal and Jalali, 2011), in concrete, e.g.

(Antonovič et al., 2010; Mukhopadhyay, 2011; Pacheco-Torgal et al., 2013; Sanchez and Sobolev, 2010) and oil industry in general, e.g. (El-Diasty and Ragab, 2013; Esmaeili, 2011; Kong and Ohadi, 2010; Li et al., 2013; Matteo et al., 2012; Ponmani et al., 2013). The present review supplementing these reviews, focuses on the application of nanotechnology for preventing cement sheath failure thereby improving long-term zonal isolation of oil wells. The factors affecting zonal isolation are introduced in Section 2, and the factors compromising long-term zonal isolation are further dealt with in Section 2.1. The required properties of a cement system to provide the desired long-term performance are discussed in Section 3. The impact of nanoadditives on the tensile properties and the bulk shrinkage of cement systems is reviewed in Section 4 and Section 5, respectively. This review is applicable for oil well cement sheaths in particular and cement-based materials in general.

2   Factors influencing zonal isolation

Primary cementing is the process of placing cement slurry in the annulus between the casing and the formation (Nelson and Guillot, 2006). The principal goal of primary cementing is to provide a complete zonal isolation in the well to ensure safety and prevent environmental problems while the well is operating economically (Hunter et al., 2007). The economic longevity of a producing oil and gas well is directly linked to the quality of the cementing job, and without complete isolation in the wellbore, the well may never reach its full production potential (Nelson and Guillot, 2006).

Numerous factors may contribute to loss of zonal isolation. The physical state of the cement system develops initially from a liquid slurry during placement, through a permeable and weak solid, to an (almost) impermeable solid after hardening (Nelson and Guillot, 2006).

The physical process of gas migration, the most common and most dangerous form of annular flow, is convenient to categorize according to when it happens during the cementing operation. Immediate gas migration (during placement), short-term gas migration, and long-term gas migration are the three major categories of gas migration during the life of the well (Nelson and Guillot, 2006). Immediate gas migration occurs from the start of the cementing job to the end of cement placement. It is essential to control the thickening time and viscosity during placement to preserve the flowability of the slurry and ensure a complete placement of slurry in the annulus. Short-term gas migration can occur anytime between a few minutes to a few days after the end of cement placement. Properties impacting zonal isolation in this period include fluid loss (filtration), free fluid development (bleeding), gel strength development, chemical shrinkage, and permeability

(Nelson and Guillot, 2006). The required short-term properties are summarized below (Nelson and Guillot, 2006; Ravi et al., 2002; Shadravan et al., 2014; Williams et al., 2011) :

- Slurry stability
    - Non-settling under static and dynamic condition
    - Limited free-fluid (bleeding) (< 0.25 vol. %)
- Limited fluid-loss (filtration) (< 50 ml/30 min)
- Static gel strength development (time to transition from 48 Pa (100 lbf/100 ft^2) or critical static gel strength to 240 Pa (500 lbf/100 ft^2) less than 45 min)
- Low permeability
- Limited chemical shrinkage during the transition phase from slurry to final set

Usually, short-term properties have been in focus by industry rather than the long-term properties. However, even when the cement slurry is placed properly and its short-term properties provide adequate zonal isolation, the long-term zonal isolation can be compromised. In general, the required long-term properties of a cement system are:

- Volume stability
- Chemical stability
- Mechanical stability under static/cyclic loads
- Thermal stability under static and cyclic thermal condition

In addition to optimal cement system performance, long-term zonal isolation requires that the drilling and cement placement procedures are done ideally, i.e. proper casing centralization, adequate mud removal, complete cement placement, adequate cement-formation/cement-casing bond, and no cement slurry contamination.

2.1 Factors compromising long-term zonal isolation

In order to identify the origin of factors leading to loss of long-term zonal isolation in cemented oil wells, the causes of problems are analyzed from the time when the cement slurry is placed in the annulus. Initially cement hydration is the main cause of distress inside the cement sheath; later the different well operations affect the stresses in the cement sheath.

Typical operations during a well's lifetime and the main influencing parameters for each operation are listed in Table 1. When designing the cement system, it is important to consider depth dependent temperature and confining pressure during and after placement (ISO10426-1, 2009) and the temperature and pressure conditions during possible later operations. All loads have a direct

influence on the radial, axial and tangential stresses to the cement sheath (Ramos et al., 2009), see Fig. 1. Most of the operations listed in Table 1 can be expressed as cyclic loading with different frequency and amplitude; thus, the cement sheath performance under cyclic loading is critically crucial compared to the case of static loading. In HPHT cyclic loading situations, tensile failure of cement sheath occurs according to the theoretical and preliminary tests (Teodoriu et al., 2013).
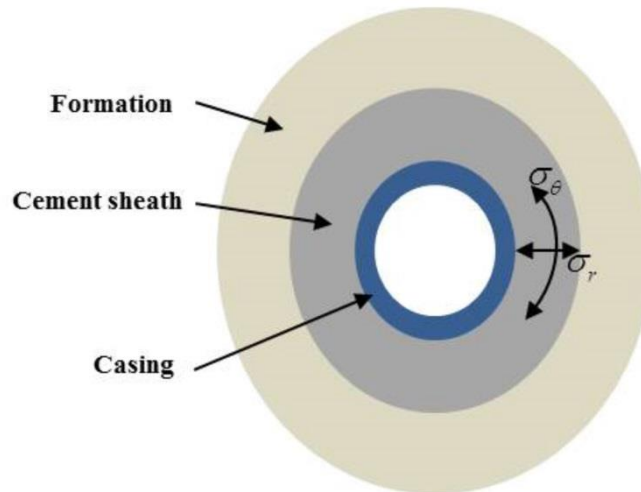

Fig. 1: Cross-section through formation, cement sheath and casing. Radial stress σ_r, and tangential stress σ_θ, are indicated, after (Thiercelin et al., 1998).

The potential failure of cemented oil wells compromising zonal isolation can be divided into three groups: formation-cement debonding (outer microannulus), casing-cement debonding (inner microannulus), and failure of cement sheath itself (Liu and Vipulanandan, 2012). Formation-cement debonding, can be caused by bulk shrinkage, incomplete mud removal, stiffness difference between formation and cement sheath and/or temperature and pressure change inside the casing. Casing-cement debonding can form due to stiffness differences and/or pressure and temperature fluctuation inside the casing. Failure of the cement sheath itself can be due to pressure and temperature fluctuations and bulk shrinkage causing tensile failure; or cyclic loads, formation pressure and formation subsidence and movement, which can lead to shear failure (Liu and Vipulanandan, 2012; Nelson and Guillot, 2006; Teodoriu et al., 2013). In general, cement sheaths fail to perform as designed mainly because of too low tensile properties and volumetric instability (McCulloch et al., 2003; Nelson and Guillot, 2006).

3   Requirements to cement systems to provide long-term zonal isolation

The ability of a cement system to provide long-term zonal isolation depends on the mechanical properties of the cement sheath, the formation, geometry of the cased wellbore and the well

condition (Thiercelin et al., 1998). As described in the previous section, cement sheaths typically fail because of volumetric instability and imposed tensile stresses beyond the tensile strength of the cement sheath.

Table 1: Possible main operations/events during the life of an oil well after cement placement, after (Hunter et al., 2007).

Operation/ events	Typical time of occurrence after cement placement	Typical duration	Main affected property/load	Range of variation/example value
Cement hydration	Start earlier	Months	Autogenous (bulk shrinkage)	Volume reduction: 1-5 % (Reddy et al., 2009)
Pressure testing	Hours	Hours	Pressure	50 MPa in a 244 mm, 69.9 kg/m casing results in a strain in the casing-formation interface of 1.25 millistrains (James and Boukhelifa, 2008)
Subsequent drilling	Days	Week	Mechanical load (shock wave), pressure, temperature	Drill string rotating at 100 rpm for 50 h Pressure variation if the mud weight has been changed to drill the next section (Thiercelin et al., 1998) Temperature increase of the cased section when the mud, which has been heated by the formation being drilled, returns to the surface via the annulus (Thiercelin et al., 1998)
Well completion	Weeks	Weeks	Pressure, temperature	
Perforation	Weeks	Day	Pressure, mechanical load (shock wave)	Pressure increase to values in excess of 40 MPa (Thiercelin et al., 1998)
Hydraulic fracturing	Years	Day (x times)	Pressure	Differential pressure: (7 to 55) MPa (Shadravan et al., 2014; Williams et al., 2011) Pressure increase is more damaging because the fluid injection lasts from minutes to hours (Thiercelin et al., 1998)
Hydrocarbon production	Year	Years	Pressure, temperature	Depends on production zone depth Pressure and temperature fluctuation mainly concerns the near-surface casing sections (Thiercelin et al., 1998)
Fluid injection	Years	Months (x times)	Pressure, temperature	Steam injection: a temperature increase of 250 ℃ results in a strain in the cement sheath at the casing interface of 3.25 millistrains (James and Boukhelifa, 2008) Injector well: Max. $P = 8$ MPa, $\Delta T = 45$ ℃ results in 420 pressure cycles from (0 to 8) MPa (Pedersen et al., 2006)
Formation movement	Decades	Hours	Mechanical load	Dependent on formation creep-characteristics

Several have suggested requirements to tensile strength, Young's modulus, and other mechanical properties of the cement sheath to provide a long-term zonal isolation through long-term stress evaluation (Bois et al., 2011; Bois et al., 2012; Roy-Delage et al., 2000; Saint-Marc et al., 2008; Stiles and Hollies, 2002). Thiercelin et al. (1998) analyzed different stress conditions in oil wells which were applicable for most types of loading. They considered wellbore pressure increase and decrease, formation pressure increase, and well temperature increase; a summary of the qualitative requirements are shown in Table 2. Due to special- and varying-conditions of each well, quantitative requirement are not generally applicable.

Table 2: Typical loading modes, stress type, stress value, max. stress location, failure mechanisms, and cement system requirement to prevent failure, after (Nelson and Guillot, 2006; Teodoriu et al., 2013; Thiercelin et al., 1998).

Loading mode	Stress value	Stress type (Fig. 1)		Max. stress location	Failure mechanism	Requirements to cement system
		Radial	**Tangential**			
Wellbore pressure increase	Linear function of wellbore pressure	Compressive	Tensile	Casing-cement interface	Tensile radial crack	Low Young's modulus
Wellbore temperature increase	Function of exposure time	Compressive	Compressive (near the casing-cement interface) Tensile (near the formation-cement interface)	Formation-cement interface	Debonding, cement sheath failure	
Wellbore pressure decrease	Linear function of wellbore pressure	Tensile	Compressive	Casing-cement interface	Debonding (location depends on the bonding strength of the two interfaces)	High tensile strength, more flexible than the formation, expansive
Wellbore temperature decrease	Function of exposure time					
Formation pressure increase	Dependent on formation creep-characteristics	Compressive	Compressive	Formation-cement interface	Buckling of the casing, shear failure under compression	High compressive strength

The tensile strength requirement strongly depends on the loading during the life of the well and the mechanical properties of the formation. The Young's modulus of the cement sheath should be lower than that of the formation to mitigate the tensile strength requirement when the wellbore pressure or temperature increase. For flexible cement sheaths, the tangential stress is less tensile

and more compressive near the casing-cement interface. This reduces the required tensile strength to prevent cracking (Thiercelin et al., 1998; Williams et al., 2011). In contrast, in case of wellbore pressure decrease, the tensile strength requirement increases with increasing Young's modulus of the formation, and debonding is more likely to occur when the cement system is placed in a stiff formation because it constrains cement deformation (Thiercelin et al., 1998). As all types of loading might be encountered in a well's life, it's important to consider an optimum Young's modulus for the cement sheath according to the formation's mechanical properties.

Each well has its special condition and a custom made design is needed. Therefore, it is necessary to determine the stresses that can occur in a well during the entire service life and identify the risks of cement sheath failure (McCulloch et al., 2003). In Table 2, it can be observed that during different loading modes a cement system with low Young's modulus is needed to survive under the imposed stresses. Moreover, the Young's modulus affects the requirements to tensile and compressive strengths, and a reduction of Young's modulus will decrease the required tensile strength to maintain zonal isolation. Consequently, two common mechanical characteristics of a cement system which can survive in oil and gas wells stress conditions are as below:

1. The ratio of cement sheath-to-formation Young's modulus: A suitable value would be 0.5 (Williams et al., 2011).
2. The ratio of tensile strength to Young's modulus σ_t/E, of cement sheath: A higher ratio is more favorable for elevated stress environments. The requirement is well-specific. (Nelson and Guillot, 2006; Williams et al., 2011)

Fig. 2 illustrates schematic load-extension curves for a target system and cement system with and without fibrous or flexible material. The target system presents a high strength and low Young's modulus illustrating the potential combined impact of fibrous and flexible additives. The target system has the potential to prevent cement sheath failure.

In addition to mechanical properties, the short-term and long-term shrinkage should be compensated effectively. Conventional cement systems without compensation for bulk shrinkage have a high risk of failure during all phases of the well operation. However, when the volume reduction is compensated without significantly modifying the mechanical properties, the risk of damage to the cement sheath is considerably reduced. Increasing the tensile strength of a conventional system without compensation for shrinkage will slightly reduce the risk of failure (McCulloch et al., 2003). As an example, for the wells located in Marcellus shale (Williams et al., 2011), application of a flexible expanding cement system providing adequate flexibility and

expansion as listed in Table 3 compensates both short-term and long-term shrinkage and provides zonal isolation during and after simulation-related stress events.
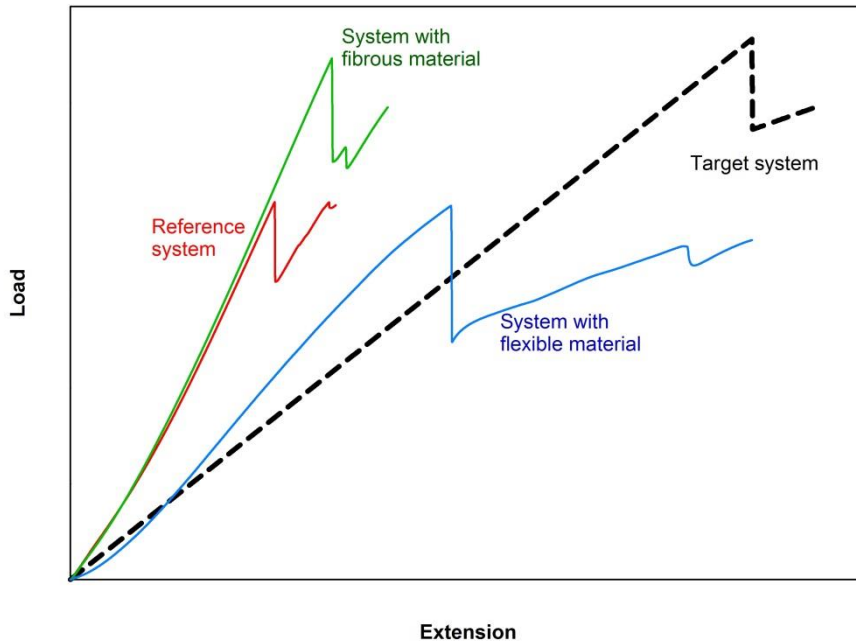

Fig. 2: Schematic load extension curve of a target system (see text) compared to the response of a reference system and systems containing fibrous or flexible particles (Own data).

Table 3: Required mechanical properties of the cement sheath providing reduced SCP[*] to prevent potential damage to the cement sheath for wells located in Marcellus shale (Williams et al., 2011).

Property	Required range
Bulk expansion (%)	0.2-0.5
Flexibility (Young's modulus , GPa)	2.4-6.2

*SCP=Sustained Casing Pressure, caused by hydrocarbon fluid migration from the formation to the surface through communication pathways in the annulus.

4   Improvement of tensile properties

To create a long-term zonal isolation, a flexible cement system exhibiting high σ_t/E with high resistance to fatigue and low shrinkage is required. The impact of nanofibers, nanoparticles, flexible particles and hybrid addition of these additives on tensile properties are discussed.

4.1   Nanotubes and nanofibers

4.1.1   Tensile strength

Addition of fibers is one of the most common and effective methods to improve the tensile behavior of cement-based materials. The impact of discrete macro- to microfibers on controlling crack growth in cement-based materials has been studied over the several decades (Berndt and Philippacopoulos, 2002).

The impact of fibers on the mechanical properties of cement-based materials primarily depends on the fiber dimension because the fracture indeed has a multi-scale nature e.g. (Metaxa et al., 2010). Macrofibers (typically defined as fibers with diameters greater than 500 μm) can improve post-peak toughness by bridging macrocracks. Fine microfibers (typically defined as fibers with diameter less than 50 μm), on the other hand, bridge the microcracks and delay microcracks coalescence to form macrocracks (Metaxa et al., 2010). However, cracks in cement-based materials initiate from the nanoscale where microfibers are not effective (Metaxa et al., 2010). Consequently, nanoscale fibers have attracted researchers over the last years (Konsta-Gdoutos et al., 2010; Li et al., 2005; Nochaiya and Chaipanich, 2011; Tyson et al., 2011).

Literature data on the impact of different nanofibers and nanotubes on the tensile strength of cement paste is summarized in Table 4. In the majority of the studies, the flexural strength was tested, but on specimens with different sizes. As discussed in Section 3, the tensile strength is the property to evaluate for assessment of the performance under induced stresses. Several equations and correlation factors have been proposed to estimate the tensile strength from the flexural strength (Balbo, 2013; Bhanja and Sengupta, 2005; Thiercelin et al., 1998). In the present paper the tensile strength of the system is determined from the flexural strength according to Eq. 1, which also includes the impact of the size of the tested specimen (Beverly, 2010).

$$\sigma_t = \sigma_{t,u} = \alpha_{sp}.\sigma_{t,sp} = \frac{0.06.h_b^{0.7}}{1 + 0.06.h_b^{0.7}}.\sigma_f \qquad\qquad Eq.1$$

where $\sigma_{t,u}$ is the mean value of the uniaxial tensile strength; $\sigma_{t,sp}$ is the mean value of the splitting tensile strength; σ_f is the mean flexural strength; h_b is the beam depth; and $\alpha_{sp} = 1.0$ has been chosen as a compromise (Beverly, 2010). σ_t is tensile strength measured using splitting tensile test, Brazilian test or calculated from flexural strength according to Eq. 1.

Among fibers in nanoscale, carbon nanotubes (CNTs) and nanofibers (CNFs) have attracted the most interest due to their extraordinary strength with Young's modulus in the order of TPa and tensile strength in the range of GPa (Sanchez and Sobolev, 2010). There are several studies on the impact of CNTs and CNFs on cement-based material properties, especially, mechanical properties as given in Table 4.

In the application of CNTs and CNFs in cement-based materials, one of the main challenges is the proper dispersion of CNTs and CNFs, partly due to their high hydrophobicity and partly due to their strong tendency to agglomerate owning to high surface area-to-volume ratio. Incorporating

CNTs or CNFs in cement systems has been proven to be rather complex and inconsistent mechanical properties of the composites have been obtained (Sanchez and Sobolev, 2010). As presented in Table 4, addition of 0.1 % multi-wall CNTs (MWCNTs) to oil well cement paste without surfactant reduced the tensile strength about 30 % compared to the control system (Santra et al., 2012); while well-dispersed CNTs resulted in significant increase in flexural strength, stiffness and deformation ability (Abu Al-Rub et al., 2012; Li et al., 2005; Metaxa et al., 2010). Addition of 0.2 % MWCNTs led to 260 % increase in the tensile strength (Abu Al-Rub et al., 2012). Studies on CNTs and CNFs emphasize that resolving the issues related to dispersion is a key issue for the application of CNTs or CNFs in cement-based materials (Sanchez and Sobolev, 2010).

Table 4: The impact of carbon nanotubes (CNTs) and nanofibers (CNFs) on tensile strength σ_t, and Young's modulus E, of cement paste.

Fiber	Content (wt. %)	Size Diameter (nm)	Length (μm)	w/c*	Curing time (d)	Flexural strength (MPa)	E (GPa)	σ_t (MPa)	$\sigma_t/\sigma_{t.Ref}$	E/E_{Ref}	Ref.
Short-MWCNT	0	20-40	10-30	0.3	28	9.3	16.4	3.1	1.00	1.00	(Konsta-Gdoutos et al., 2010)
	0.048					10.8	-	3.5	1.13	-	
	0.08					12.7	21.9	4.2	1.35	1.34	
	0.1					11.5	-	3.8	1.23	-	
Short-MWCNT	0	9.5	1.5	0.4	28	3.3	14.5	0.6	-	-	(Abu Al-Rub et al., 2012)
	0.04					3.8	12.2	0.7	1.17	0.84	
	0.1					4.5	15.2	0.8	1.33	1.05	
	0.2					11.9	17	2.2	3.67	1.17	
Long-MWCNT	0	20-40	10-100	0.3	28	9.3	16.4	3.1	1.00	1.00	(Konsta-Gdoutos et al., 2010)
	0.025					11.5	21.9	3.8	1.23	1.34	
	0.048					11.5	20.2	3.8	1.23	1.23	
	0.08					10.2	-	3.3	1.06	-	
Long-MWCNT	0	< 8	10-30	0.4	28	3.3	14.5	0.6	1.00	1.00	(Abu Al-Rub et al., 2012)
	0.04					5	15.2	0.9	1.5	1.05	
	0.1					5.3	13.0	1.0	1.67	0.90	
CNF	0	60-150	30-100	0.5	28	5.5	8.8	1.8	1.00	1.00	(Metaxa et al., 2010)
	0.048					7.2	13.2	2.4	1.33	1.5	
MWCNT	0	13-18	3-30	0.54	7	-	7.2	2.6	1.00	1.00	(Santra et al., 2012)
	0.1					-	7.1	1.8	0.69	0.99	
	0.2					-	7.2	2.5	0.96	1.00	

* Water-to-cement mass ratio

4.1.2 Flexibility

Addition of fibers into cement paste will change the Young's modulus, which characterizes the flexibility of a material. In most studies, addition of fibers was found to increase the Young's modulus, tensile strength, and toughness of the cement system, see Table 4. Addition of CNTs and CNFs showed mixed result; in a few cases a small decrease in Young's modulus was observed

while in most of the systems Young's modulus increased. Addition of 0.2 % by weight of cement, fibrous nanoclay resulted in about 50 % and 20 % increase in tensile strength and Young's modulus, respectively (Jafariesfad et al., 2015).

Tensile strength and toughness improvement are favorable for oil well cement system. However, as discussed in Section 3, Young's modulus also affects the tensile strength requirement. For the wells located in the Marcellus shale, the preference is to reduce the Young's modulus to the values in the range of 2.4-6.2 GPa, depending on well and formation requirements (Williams et al., 2011). This range values is unreachable by addition of only very stiff fibers like CNTs and CNFs.

4.2   Nanoparticles

Nanoparticles having a very high surface area-to-volume ratio can act as nuclei for cement hydrates promoting cement hydration (Lindgreen et al., 2008; Pang et al., 2014). As reinforcement and as filler, they are densifying the microstructure resulting in a reduced porosity (Sanchez and Sobolev, 2010). Distribution of nanoparticles in cement slurry also increases the matrix viscosity (Choolaei et al., 2012), which might impair the homogeneous dispersion of nanoparticles in the slurry. For all nanoparticles, the most significant problem is to achieve a homogeneous dispersion, which depends on a few critical factors such as concentration, matrix viscosity and attractive forces (Parveen et al., 2013). High nanoparticle concentration leads to relatively high agglomeration tendency (Sanchez and Sobolev, 2010) and increased viscosity of the cement slurry. Potential properties of nanocomposite can only be achieved by an effective dispersion of nanoparticles in the matrix (Parveen et al., 2013). It has been observed that addition of 5 % (Stefanidou and Papayianni, 2012) and 3 % of nano-SiO_2 and 5 % of TiO_2 (Li et al., 2006) decreased the flexural strength of the concrete. This was attributed to the weak zones caused by agglomeration of nanoparticles.

The impact of addition of nanosized particles on tensile strength of cement mortar and paste are summarized in Table 5. Addition of 5 % nanosized bentonite to oil well cement paste resulted in 54 % increase in tensile strength compared to a reference mixture with microsized bentonite (Roddy et al., 2013). Fig. 3 illustrates the impact of various metal oxide nanoparticles with the same size, on tensile strength of concrete with water-to-binder mass ratio (w/b) of 0.4 after 28 days of curing. System containing 4 % nano-SiO_2 showed significant enhancement in tensile strength (Nazari and Riahi, 2011c). SiO_2 (Nazari and Riahi, 2011c), TiO_2 (Nazari and Riahi, 2011d) and ZnO_2 (Nazari and Riahi, 2011e) nanoparticles performed similarly in concrete . Up to 4 % increase in nanoparticle content resulted in tensile strength enhancement, but beyond 4 % led to tensile strength reduction. The optimum concentration for system containing Al_2O_3 (Nazari and Riahi,

2011a) and Cr_2O_3 (Nazari and Riahi, 2011b) was 1 %. In almost all of the studies, addition of nanoparticles in relatively low concentrations resulted in noticeable tensile strength improvement. However, still there is lack of information about their impact on Young's modulus (Nazari and Riahi, 2011a; Nazari and Riahi, 2011b; Nazari and Riahi, 2011c; Nazari and Riahi, 2011d; Nazari and Riahi, 2011e).

Table 5: The impact of nanosized particles on tensile strength σ_t, and Young's modulus E, of cementitious systems.

Particle	Content (wt. %)	Size	w/b	System type	Curing time (d)	Flexural strength (MPa)	σ_t (MPa)	$\sigma_t/\sigma_{t.Ref}$	Ref.
Bentonite	5	32-38 µm	-	Paste	3	-	1.1	-	(Roddy et al., 2013)
Nanobentonite	5	-				-	1.7	1.54**	
Nanoclay platelets	0	-	0.48	Paste	56	5.4	1.5	-	(Hakamy et al., 2014)
	1					7.2	2.1	1.40	
	2					7.1	2.0	1.33	
	3					6.8	1.9	1.27	
Nano- SiO₂	0	15 nm	0.5	Mortar	28	4.9	2.2	-	(Li et al., 2004)
	3					5.8	2.6	1.18	
	5.2					6.2	2.7	1.23	
Nano-MgO	0	30 nm	0.5*	Mortar	28	3.0	1.1	-	(Moradpour et al., 2013)
	1					5.1	1.9	1.73	
	3					3.5	1.3	1.18	
	5					3.2	1.2	1.09	
Nano-Fe₂O₃	0	30 nm	0.5	Mortar	28	4.9	2.2	-	(Li et al., 2004)
	3					5.8	2.6	1.18	
	5.2					6	2.7	1.23	

* w/c

** Reference system contained the same content of bentonite in microscale (32-38 µm)
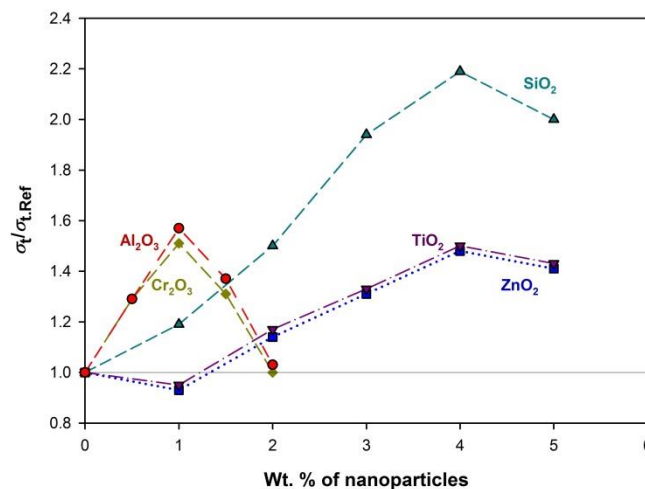

Fig. 3: The impact of nanoparticles with average size of 15 nm on tensile strength of concrete with w/b of 0.4, at the age of 28 days of curing, data from (Nazari and Riahi, 2011a; Nazari and Riahi, 2011b; Nazari and Riahi, 2011c; Nazari and Riahi, 2011d; Nazari and Riahi, 2011e).

In addition to long-term properties, presence of nanoparticles in cement slurry has a major impact on its short-term properties which should be considered in designing cement system. Thickening time, slurry stability (free-fluid, sedimentation and fluid-loss), rheological properties, gel strength development, porosity and permeability are strongly influenced by concentration and type of nanoparticles. Incorporation of nano-SiO_2 to oil well cement slurry resulted in zero free-fluid, significant reduction in dormant period, and reduced porosity and permeability (Choolaei et al., 2012).

4.3   Flexible particles

Flexible particles have been used to increase the flexibility of the cement-based system. Suggested characteristics of flexible particles eligible to be used in cement system are (Roy-Delage and Thiercelin, 2004):

1.   Particle size ≤ 500 µm
2.   Density less than 1500 kg/m^3,
3.   Young's modulus < 5 GPa, preferably < 2 GPa ,
4.   0.3 < Poisson's ratio < 0.45

Several polymeric materials conform to these performance criteria. Examples are thermoplastics like polyamide, polypropylene and polyethylene, styrene divinylbenzene or styrene butadiene (Roy-Delage and Thiercelin, 2004). While these materials can provide flexible cement systems resistant to induced stresses due to pressure and temperature fluctuations, problems can occur if the well is also exposed to high temperatures like what can be encountered in steam injection wells or geothermal wells. The mentioned polymeric materials are not suitable for high temperature applications as they either melt or deteriorate at high temperatures. There are several thermoplastics (PEEK, Ryton, PTFE) which are stable at high temperatures and in highly alkaline environments (as occur in cement slurry), but their cost is prohibitive for massive applications in well cementing (Roy-Delage and James, 2008).

Addition of conventional microsized flexible particles into cement system results in reduction of the Young's modulus, but also the tensile strength. It is necessary to find materials which improve both flexibility and tensile strength, or at least increase σ_t/E so that cement system is capable of maintaining zonal isolation under extreme stress condition. Such materials could be flexible particles in nanoscale. Epoxy resin exhibit inherent brittle nature and poor crack resistance somehow similar to cementitious materials. Incorporation of microsized rubber particles used as a method to improve the toughness of epoxy composites, but also they lead to significant loss of

tensile strength (Thomas et al., 2008). Compared to the microrubber, the nanorubber particles produce an impressive toughening effect, while preserve the tensile properties of epoxy (Tang et al., 2013). It has been observed that incorporation of performed nanoscale powdered rubber particles (PR) into epoxy resin resulted in increased or almost unchanged tensile yield strength of the cured epoxy/PR composites (Guan et al., 2015; Tang et al., 2013). Therefore, partial or total replacement of conventional flexible particles by their nanoscale version can be the promising solution to improve the flexibility while keeping the tensile strength of cement system.

In addition to flexibility improvement, incorporation of rubber particle into both concrete and oil well cement systems is a common method to improve resistance to shocks and cyclic loads (Dargaud et al., 2003; Nelson and Guillot, 2006; Sukontasukkul and Chaikaew, 2006). Thus, improvement of the cement system flexibility can result in a system which is capable of standing under cyclic loads.

4.4 Hybrid additives

In a hybrid, two or more different types of additives are combined to create a composite that derives benefits from each of the individual additives and exhibits a synergistic response. Addition of fiber-toughening agents is a common way to improve tensile strength and toughness of cement systems. However, the Young's modulus is barely decreased and the flexibility is hardly improved (Yao and Hua, 2007). Therefore, it is necessary to develop additives that are able to improve flexibility, tensile strength and toughness, while not negatively affecting the other engineering properties of cement systems.

Table 6 presents different hybrid composites in an attempt to produce a flexible cement system while keeping the tensile strength unaltered. It could be found that addition of flexible agents such as rubber particles or latex resulted in Young's modulus reduction and flexibility improvement, but reduced tensile strength as well. A hybrid use of flexible agents with fibers in most of the cases led to simultaneous improvement in tensile strength and flexibility. Recently, the combination of nanoparticles/nanofibers with polymeric materials in cement-based materials has been used to improve ductility and provide high mechanical properties. Metaxa et al. (2010) used CNF, polyvinyl alcohol (PVA) microfibers and their combination aiming to improve tensile strength and toughness in cementitious matrix. By addition of only 0.048 wt. % CNFs, the flexural strength and the Young's modulus of cement matrix increased up to 40 % and 75 %, respectively. Conversely, adding 0.54 wt. % PVA microfibers enhanced only the post-peak behavior of cement paste resulting in a highly ductile behavior. Interestingly, the combination of CNFs and PVA improved

the flexural strength up to 50 % and toughness up to 33 times (3350 %) of the cementitious matrix. It resulted in stronger and tougher material compared to the singly-reinforced composites or plain cement paste (Metaxa et al., 2010). Incorporation of modified polypropylene fibers with well-distributed nanosilica into the cement paste showed excellent mechanical properties and crack resistance (Yang et al., 2011); while a hybrid CNF and silica fume cement composite did not show any difference compared to neat cement paste. The CNFs embedded in the paste offset the effect of defects generated by pockets of CNFs and silica fume agglomerates, resulted in no net change in the compressive and splitting tensile strengths of the composites (Sanchez and Ince, 2009). Performance enhancement of cement composites was expected if better dispersion of the CNFs in the cement paste could be achieved by surface treatment of CNFs, optimum physical blending, and/or the use of surfactants (Sanchez and Ince, 2009).

Table 6: The impact of separate or combined use of fibers and polymers on tensile strength and Young's modulus of cement paste.

Additive	Content (wt. %)	w/c	Curing time (d)	Flexural strength (MPa)	E (GPa)	σ_t (MPa)	$\sigma_t/\sigma_{t.Ref}$	E/E_{Ref}	Ref.
Reference	0	0.44	2	-	6.3	1.9	1.00	1.00	(Morris et al., 2003)
Polymer fiber (PF)	0.4	0.44		-	2.6	3.2	1.68	0.41	
Styrene-butadiene latex (L)	10	0.34		-	2.6	1.8	0.95	0.41	
Hybrid	**0.4 PF+10 L**	**0.34**		**-**	**2.5**	**3.4**	**1.79**	**0.40**	
Reference	0	0.44	2	8.3	12.6	1.9	1.00	1.00	(Yao and Hua, 2007)
Carboxylated nitrile rubber (CNR)	6			6.5	7.8	1.5	0.79	0.62	
Polypropylene fiber (PP)	0.25			8.4	14.5	1.9	1.00	1.15	
Hybrid	**5.5 CNR+0.2 PP**			**8.2**	**8.1**	**1.9**	**1.00**	**0.64**	
Reference	0	0.35	14	-	-	3.3	1.00	-	(Brothers, 2005)
Carbon fiber (CF)	5			-	-	3.5	1.06	-	
Rubber particle (R)	20			-	-	0.4	0.12	-	
Hybrid	**5 CF+20 R**			**-**	**-**	**2.1**	**0.64**	**-**	
Reference	0	0.5	28	5.5	8.8	1.8	1.00	1.00	(Metaxa et al., 2010)
CNF	0.048			7.2	13.2	2.4	1.33	1.50	
Polyvinyl alcohol (PVA)	0.54			5.8	8.9	1.9	1.05	1.01	
Hybrid	**0.048 CNF+0.54 PVA**			**7.3**	**14.6**	**2.4**	**1.33**	**1.66**	

4.5   Tensile strength requirement vs. Young's modulus

As stated in Section 3, the tensile strength of the cement system is affected by Young's modulus of both the cement system and the formation. Thiercelin et al. (1998) carried out the finite element analysis to predict the tensile strength requirement. They considered three types of loading, temperature increase of approximately 100 ^{o}C (200 ^{o}F, corresponding to 93 ^{o}C), pressure increase of 34 MPa (4900 psi), or pressure decrease of 28 MPa (4000 psi). In their simulation, the formation's Young's modulus was estimated 17 GPa in the case of pressure fluctuation, which was a mean value accounted for both possible pressure decrease and increase. In the case of temperature increase, the formation's Young's modulus of 2 GPa was used, which could be considered the minimum support from formation. For three types of loading, the requirement for tensile strength of the cement system as a function of its Young's modulus is plotted as solid curves in Fig. 4. The reference system used in the three curves has a tensile strength of 3.9 MPa and Young's modulus of 6.4 GPa (Thiercelin et al., 1998). The properties of cement systems have to fall in the upper area of each curve for the corresponding loading type. In order to ensure that the cement system survives from induced stresses from all loading types it should lie in the light green colored area. The requirements for cement sheath in Marcellus shale according to Williams et al. (2011) is indicated by the dark green area between two dash lines in Fig. 4. For a given cement system containing nanomaterials, the correlation between the relative tensile strength and the relative Young's modulus can be first determined and compared with Fig. 4. The cement systems with their properties falling in the colored area are preferable for zonal isolation.

Other literature data are normalized to the tensile strength and Young's modulus of the reference cement systems used in each study, and summarized also in Fig. 4. Based on the three requirement curves, one can see that all of the systems might experience stresses by pressure increase without failure. Several cases can encounter stresses by pressure decrease without failure. However, only a few of the cement systems fall in the colored area, which present higher degree of flexibility fulfilling the tensile strength requirement at different loading conditions. As shown in Fig. 4, systems containing CNTs and CNFs have a higher Young's modulus compared to their reference system, requiring in higher tensile strength.

5   Reduction of shrinkage

Autogenous shrinkage is defined as the self-inflicted bulk shrinkage of cement-based materials. The reaction between water and cement is associated with a reduction in volume because the reaction products fill less than the reactants. This is called chemical shrinkage and is a fundamental property of cement hydration, see e.g. (Geiker, 2015). Due to hydration, pore water is consumed

and after the plastic state the pore structure is partly empty, known as self-desiccation which creates a capillary force and an under-pressure in the pore water. The pressure is transferred to the solid and results in external contraction of the cement-based material, called autogenous or bulk shrinkage (Lura et al., 2003).
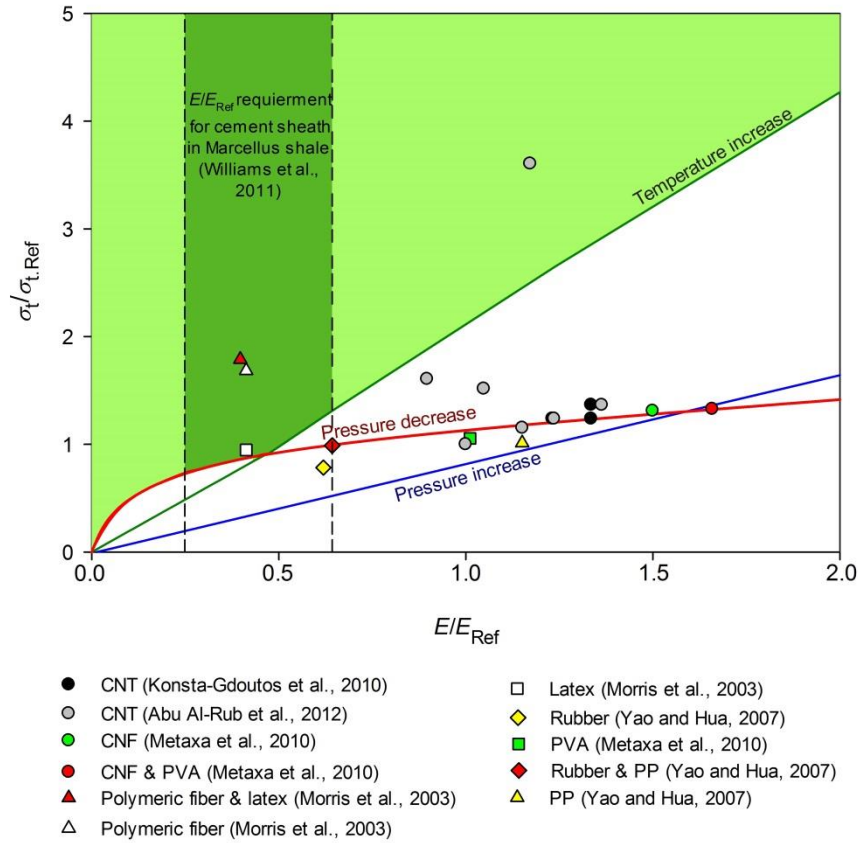

Fig. 4: Normalized tensile strength requirement vs. normalized Young's modulus of cement system for different loading types. The colored area indicates the requirements to tensile strength for all three loading conditions described by the requirement curves (solid curves): 1) Temperature increase: 93 °C (200 °F), $E_{Formation}$=2 GPa; 2) Pressure increase: 34 MPa (4900 psi), $E_{Formation}$=17 GPa; 3) Pressure decrease: 28 MPa (4000 psi), $E_{Formation}$=17 GPa (Thiercelin et al., 1998). The points present cement systems with different additives. Reference systems: for requirement curves σ_t=3.9 MPa and E=6.4 GPa (Thiercelin et al., 1998); for dashed lines σ_t=3.0 MPa and E=9.6 GPa (Williams et al., 2011); and for points see Table 4 and 6.

Bulk shrinkage of cement systems is one of the main reasons for microannuli formation compromising zonal isolation (Reddy et al., 2009). As described in Section 3, bulk shrinkage compensation of cement systems in oil wells will reduce the risk of failure due to imposed stresses (assuming no other impact on mechanical properties). Several methods are used in order to prevent or reduce shrinkage of cement-based systems, including shrinkage reducing admixtures (SRA) (Bentz et al., 2001; Sant et al., 2011), expansive additives (Ghofrani and Plack, 1993; Nelson and Guillot, 2006) and internal curing (Kovler et al., 2007).

5.1 Internal curing

In order to reduce internal stresses and strains resulting from autogenous shrinkage, additional curing water can be provided through addition of small water reservoirs, e.g. superabsorbent polymer (SAP) particles or saturated lightweight fine aggregates (LWA), e.g. (Bentur et al., 2001; Bentz and Weiss, 2011; Jensen and Hansen, 2001; Kovler et al., 2007).

SAP, also called hydrogels, are cross-linked polymers with a high liquid adsorption capacity swelling substantially and forming a soft and insoluble gel. During hydration, the adsorbed water is released and the SAP shrinks, leaving behind small macro-pores (Van Tittelboom and De Belie, 2013).

Additionally, the effectiveness of wood-based fibers and powders (Mohr et al., 2005) and cellulose fibers (Kawashima and Shah, 2011) to provide internal curing water has been assessed. Results have shown the effectiveness of certain wood-derived materials at mitigating autogenous shrinkage (Mohr et al., 2005). Cellulose fibers have internal curing capabilities. However, due to their relatively low absorption capacity, high amounts of fibers are necessary to provide enough internal curing water to show a substantial reduction in autogenous shrinkage. The obvious advantage of fibers used as internal curing agent over LWA and SAP is that they have the additional potential to provide crack resistance. (Mohr, 2005)

Recently, it has been proposed that nanoclay can serve as an internal water reservoir. The water retaining capacity of nanoclay can be used to provide extra water for further hydration (Qian et al., 2010). Addition of 1.5 wt. % and 3 wt. % clay nanoparticles to the cement mortar with a w/b of 0.3, was found to reduce autogenous shrinkage 43 % and 40 % at the age of 28 days of curing, respectively. However, the system contained 4.5 wt. % nanoclay revealed 1.5 % increased shrinkage compared to control system (Polat et al., 2015). At lower concentrations of nanoclay, internal curing might be the dominant mechanism, but at higher concentrations other mechanisms like pore filling/pore refinement (Sadrmomtazi and Fasihi, 2012) and nucleation (Camiletti et al., 2013; Jayapalan et al., 2010) could be dominant. In general, for internal curing by nanoclays, it's necessary to consider their water adsorption capacity and chemical structure (Polat et al., 2015).

5.2 Shrinkage reducing admixture (SRA)

Shrinkage reducing admixtures (SRA) reduces the surface tension of pore solution. The reduction in the surface tension of the pore solution mitigates the development of capillary stresses and maintains a high internal relative humidity resulting in reduced shrinkage (Bentz et al., 2001; Sant et al., 2011). In several studies of the impact of SRA on autogenous shrinkage, addition of SRA

reduced the autogenous shrinkage; the reduction value varied based on the SRA dosage and the mix proportions, e.g. (Arezoumandi, 2015; Cheung and Leung, 2011; Rongbing and Jian, 2005; Saliba et al., 2011; Sant et al., 2011). Application of SRA in oil well cement slurries has been found to improve the interfacial sealing and bonding between cement sheath and contacting surfaces, i.e. casing and formation, in addition to autogenous shrinkage reduction from about 10 % to 75 % during setting and hardening (Cowan, 1991).

The studies on autogenous shrinkage indicate that SRA can lead to a period of expansion which initiates shortly after the time of set, resulting in shrinkage mitigation (Weiss et al., 2008). Sant et al. (2011) suggested that this expansion might be caused by the amplification in portlandite oversaturation and its crystallization.

5.3 Expansive additives

Expanding cements, containing expansive additives, has been considered as a solution for improving sealing efficiency and prevention of microannuli formation in oil wells. There are two known effective mechanisms of matrix expansion (Ghofrani and Plack, 1993; Nelson and Guillot, 2006):

1. Crystal growth: This mechanism relies upon the nucleation and growth of certain mineral species within the cement system.
2. Gas generation: This mechanism relies upon the generation of hydrogen gas by the reaction of Mg, Al or Zn powder with the alkaline constituents of the cement system. Gas-generating systems are to be carefully stabilized; otherwise, gas bubbles may coalesce and create channels for formation fluid to flow (Nelson and Guillot, 2006).

CaO-type and sulfoaluminate-type expansive additives cause mainly early stage expansion; therefore, long-term shrinkage would not be compensated (Mo et al., 2010). Calcium sulfoaluminate requires large quantities of water for its hydration product ettringite to form (Nagataki and Gomi, 1998), otherwise it's reaction is hindered. The major limitation for use in cement sheaths of expansive systems, which rely upon the formation of ettringite, is its instability at temperatures above 76 ℃ (Nelson and Guillot, 2006).

Compared to the above-mentioned additives, MgO hydration can be controlled to compensate long-term shrinkage. In both the construction and the oil industry, MgO has been used as an expansive agent in cement systems to compensate autogenous and thermal shrinkage. Its expansion depends on the calcining temperature, residence time, particle size, and cement paste curing condition. It

must be calcined at very high temperatures to create low-reactive MgO. (Mo et al., 2010) The expansion of nanosized MgO particles can through synthesis and heat-treatment processes be controlled more precisely than conventional MgO sources. Therefore, their expansive property can be designed to compensate shrinkage in a wide range of temperatures and at different ages (Jafariesfad et al., 2016).

The grain size of expansive agents has a major impact on the autogenous shrinkage of cementitious materials. The capacity of nano- and microsized MgO and CaO in compensating autogenous shrinkage of cement mortar at 20 ℃ is illustrated in Fig. 5. Nano-MgO resulted in a major reduction in autogenous shrinkage compared to nano-CaO, mostly because the nano-CaO reacted very fast and the main reaction occurred before initial setting. Nano-MgO reacts slower than nano-CaO and it can more effectively compensate long-term shrinkage. It can be seen in Fig. 5 that micro-CaO and nano-MgO presented almost the same effect on the reduction of autogenous shrinkage at testing temperature of 20 ℃. (Polat et al., 2015) However, for application at elevated temperatures and pumping the cement slurry to great depths in oil wells, MgO is more efficient compared to CaO. In comparison with MgO, CaO exhibits a considerably higher free enthalpy and thus a higher reactivity, even in the dead-burnt state (Ghofrani and Plack, 1993). In summary, CaO-type expansive additive were reported most efficient at lower temperatures (about 50 ℃) and might hardly find applications in conditions of wellbore temperature above 80 ℃ (Appah and Reichetseder, 2002).
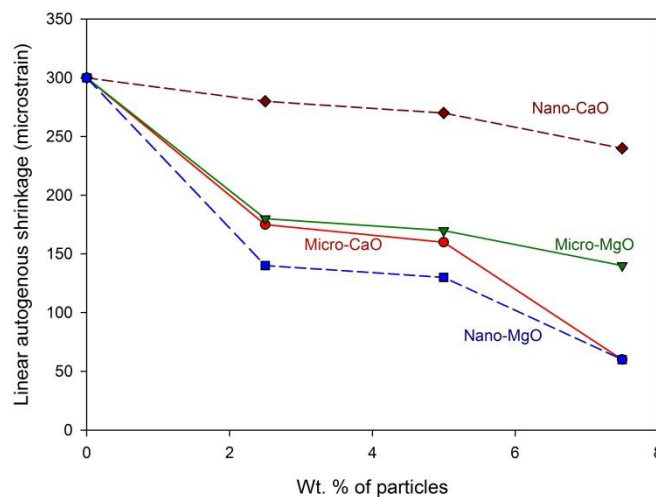

Fig. 5: The impact of MgO and CaO particle size on autogenous shrinkage of cement mortar at 28 days of curing, after (Polat et al., 2015).

Unsoundness is the increase of volume occurring after the cement paste has set, which may result in expansive cracking and loss of mechanical properties. This must be considered when using

expansive additives in a cement system. According to the ASTM standards for soundness evaluation of cement, the autoclave expansion is limited to 0.8 % (ASTM-C150/C150M−15, 2015). Investigating cementitious system containing 1 % to 5 % MgO nanoparticles by the weight of binder, Moradpour et al. (2013) observed expansion below the unsoundness limit as well as increased compressive and flexural strengths, see Table 5.

Conclusions

Long-term zonal isolation is crucial in oil well cementing. In general, cement sheaths fail to perform as designed mainly because of too low tensile properties and/or volumetric instability. Due to the uniqueness of each oil well, it is challenging to define quantitative requirement for cement systems. To limit loss of zonal isolation, a high ratio of tensile strength to Young's modulus and low Young's modulus are required. Different morphology and size of reinforcement materials are used to improve the mechanical properties of cement systems. Their effects on tensile strength, Young's modulus, and bulk shrinkage have been discussed. It is found that nanomaterials may have a major impact on the mechanical performance of cement systems. Nanosized MgO appears promising due to high thermal stability of its hydration product, adjustable expansion property according to well condition and modifying mechanical properties of cement system. Incorporation of nanosized flexible particles might be the potential solution to improve the flexibility and toughness and preserve the tensile strength of the cement system. Application of nanomaterials in oil well cement systems can be the future direction for an engineered target cement sheath providing zonal isolation during the whole well's life. A target cement system, applicable in various oil wells' conditions, might be achieved by hybrid use of nanomaterials.

Acknowledgements

References

Abdo, J. and Haneef, M.D., 2013. Clay nanoparticles modified drilling fluids for drilling of deep hydrocarbon wells. Appl. Clay Sci., 86: 76-82. http://dx.doi.org/10.1016/j.clay.2013.10.017.

Abu Al-Rub, R.K., Ashour, A.I. and Tyson, B.M., 2012. On the aspect ratio effect of multi-walled carbon nanotube reinforcements on the mechanical properties of cementitious nanocomposites. Constr. Build. Mater., 35: 647-655. http://dx.doi.org/10.1016/j.conbuildmat.2012.04.086.

Andersen, M.M. and Geiker, M.R., 2009. Nanotechnologies for climate friendly construction–key issues and challenges, Nanotechnology in Construction 3. Springer, pp. 199-207. http://dx.doi.org/10.1007/978-3-642-00980-8_27.

Antonovič, V., Pundiene, I., Stonys, R., Česniene, J. and Kerienė, J., 2010. A review of the possible applications of nanotechnology in refractory concrete. J. Civ. Eng. Manag., 16(4): 595-602. http://dx.doi.org/10.3846/jcem.2010.66.

Appah, D. and Reichetseder, P., 2002. Practical improvements in CaO-swelling cements. J. Petroleum Sci. Eng., 36(1-2): 61-70. http://dx.doi.org/10.1016/S0920-4105(02)00251-6.

Arezoumandi, M., 2015. Feasibility of crack free reinforced concrete bridge deck from materials composition perspective: a state of the art review. Front. Struct. Civ. Eng., 9(1): 91-103. http://dx.doi.org/10.1007/s11709-015-0274-1.

ASTM-C150/C150M−15, 2015. Standard Specification for Portland Cement. ASTM International, USA.

Balbo, J.T., 2013. Relations between indirect tensile and flexural strengths for dry and plastic concretes. Revista IBRACON de Estruturas e Materiais, 6(6): 854-874. http://dx.doi.org/10.1590/S1983-41952013000600003

Bentur, A., Igarashi, S. and Kovler, K., 2001. Prevention of autogenous shrinkage in high-strength concrete by internal curing using wet lightweight aggregates. Cem. Concr. Res., 31(11): 1587-1591. http://dx.doi.org/10.1016/S0008-8846(01)00608-1.

Bentz, D.P., Geiker, M.R. and Hansen, K.K., 2001. Shrinkage-reducing admixtures and early-age desiccation in cement pastes and mortars. Cem. Concr. Res., 31(7): 1075-1085. http://dx.doi.org/10.1016/S0008-8846(01)00519-1.

Bentz, D.P. and Weiss, W.J., 2011. Internal curing: a 2010 state-of-the-art review. US Department of Commerce, National Institute of Standards and Technology.

Berndt, M.L. and Philippacopoulos, A.J., 2002. Incorporation of fibres in geothermal well cements. Geothermics, 31(6): 643-656. http://dx.doi.org/10.1016/S0375-6505(02)00028-7.

Beverly, P., 2010. fib Model Code for Concrete Structures 2010. Wilhelm Ernst & Sohn, Germany. http://dx.doi.org/10.1002/9783433604090.

Bhanja, S. and Sengupta, B., 2005. Influence of silica fume on the tensile strength of concrete. Cem. Concr. Res., 35(4): 743-747. http://dx.doi.org/10.1016/j.cemconres.2004.05.024.

Bois, A.P., Gamier, A., Rodot, F., Saint-Marc, J. and Aimard, N., 2011. How to prevent loss of zonal isolation through a comprehensive analysis of microannulus formation. SPE Drill. Completion, 26(1): 13-31. http://dx.doi.org/10.2118/124719-PA.

Bois, A.P., Garnier, A., Galdiolo, G. and Laudet, J.B., 2012. Use of a Mechanistic Model To Forecast Cement-Sheath Integrity. SPE Drill. Completion, 27(2): 303-314. http://dx.doi.org/10.2118/139668-PA.

Brothers, L.E., 2005. Cement compositions with improved mechanical properties and methods of cementing in subterranean formations. Google Patents.

Camiletti, J., Soliman, A. and Nehdi, M., 2013. Effects of nano-and micro-limestone addition on early-age properties of ultra-high-performance concrete. Mater. Struct., 46(6): 881-898. http://dx.doi.org/10.1617/s11527-012-9940-0.

Cheung, A.K. and Leung, C.K., 2011. Shrinkage reduction of high strength fiber reinforced cementitious composites (HSFRCC) with various water-to-binder ratios. Cem. Concr. Compos., 33(6): 661-667. http://dx.doi.org/10.1016/j.cemconcomp.2011.03.009.

Choolaei, M., Rashidi, A.M., Ardjmand, M., Yadegari, A. and Soltanian, H., 2012. The effect of nanosilica on the physical properties of oil well cement. Mater. Sci. Eng. A-Struct. Mater. Prop. Microstruct. Process., 538: 288-294. http://dx.doi.org/10.1016/j.msea.2012.01.045.

Cowan, K.M., 1991. Cement sealing. Google Patents.

Dargaud, B., Roy-Delage, S.L. and Thiercelin, M., 2003. Cementing compositions and application of such compositions for cementing oil wells or the like. Google Patents.

Del Gaudio, L., Bortolo, R. and Lockhart, T.P. 2007. Nanoemulsions: a new vehicle for chemical additive delivery. Proc., International Symposium on Oilfield Chemistry, Houston, Texas, 28 February–2 March. http://dx.doi.org/10.2118/106016-MS.

El-Diasty, A.I. and Ragab, A.M.S. 2013. Applications of Nanotechnology in the Oil & Gas industry: Latest Trends Worldwide & Future Challenges in Egypt. Proc., North Africa Technical Conference and Exhibition, Cairo, Egypt, 15–17 April. http://dx.doi.org/10.2118/164716-MS.

Esmaeili, A. 2011. Applications of Nanotechnology in Oil and Gas Industry. Proc., American Institute of Physics Conference Series, New Dehli, India.

Geiker, M.R., 2015. Characterisation of development of cement hydration using chemical shrinkage. In: K. Scrivener, R. Snellings and B. Lothenbach (Editors), A Practical Guide to Microstructural Analysis of Cementitious Materials. CRC Press, pp. 75-106.

Ghofrani, R. and Plack, H. 1993. CaO- and/or MgO-Swelling Cements: A Key for Providing a Better Annular Sealing? Proc., SPE/IADC Drilling Conference, Amsterdam, 23-25 February. http://dx.doi.org/10.2118/25697-MS.

Guan, L.-Z. et al., 2015. Mechanical properties and fracture behaviors of epoxy composites with phase-separation formed liquid rubber and preformed powdered rubber nanoparticles: A comparative study. Polym. Compos., 36(5): 785-799. http://dx.doi.org/10.1002/pc.22995.

Hakamy, A., Shaikh, F. and Low, I., 2014. Thermal and mechanical properties of hemp fabric-reinforced nanoclay–cement nanocomposites. J. Mater. Sci., 49(4): 1684-1694. http://dx.doi.org/10.1007/s10853-013-7853-0.

Hanus, M.J. and Harris, A.T., 2013. Nanotechnology innovations for the construction industry. 58(7): 1056-1102.

Hunter, B., Ravi, K. and Kulakofsky, D. 2007. Three Key Mechanisms Deliver Zonal Isolation. Proc., IADC Drilling Gulf of Mexico Conference and Exhibition, Galveston, Texas.

ISO10426-1, 2009. Petroleum and natural gas industries-Cements and materials for well cementing-Part1: Specification. ISO, Geneva, Switzerland.

Jafariesfad, N., Gong, Y., Geiker, M.R. and Skalle, P. 2015. Impact of ultrafine fibrous clay on tensile properties of oil well cement systems. Proc., ICCC2015, Beijing, China.

Jafariesfad, N., Gong, Y., Geiker, M.R. and Skalle, P. 2016. Nano-Sized MgO with Engineered Expansive Property for Oil Well Cement Systems. Proc., SPE Bergen One Day Seminar, Norway, 20 April. http://dx.doi.org/10.2118/180038-MS.

James, S.G. and Boukhelifa, L., 2008. Zonal Isolation Modeling and Measurements - Past Myths and Today's Realities. SPE Drill. Completion, 23(1): 68-75. http://dx.doi.org/10.2118/101310-PA.

Jayapalan, A.R., Lee, B.Y., Fredrich, S.M. and Kurtis, K.E., 2010. Influence of Additions of Anatase TiO2 Nanoparticles on Early-Age Properties of Cement-Based Materials. J. Transp. Res. Board, 2141: 41-46. http://dx.doi.org/10.3141/2141-08.

Jensen, O.M. and Hansen, P.F., 2001. Water-entrained cement-based materials: I. Principles and theoretical background. Cem. Concr. Res., 31(4): 647-654. http://dx.doi.org/10.1016/S0008-8846(01)00463-X.

Jimenez, W.C. et al. 2016. Innovation of Annular Sealants During the Past Decades and Their Direct Relationship with On/Offshore Wellbore Economics. Proc., SPE Bergen One Day Seminar, Bergen, Norway, 20 April. http://dx.doi.org/10.2118/180041-MS.

Kawashima, S. and Shah, S.P., 2011. Early-age autogenous and drying shrinkage behavior of cellulose fiber-reinforced cementitious materials. Cem. Concr. Compos., 33(2): 201-208. http://dx.doi.org/10.1016/j.cemconcomp.2010.10.018.

Kong, X. and Ohadi, M. 2010. Applications of micro and nano technologies in the oil and gas industry-overview of the recent progress. Proc., Abu Dhabi international petroleum exhibition and conference, Abu Dhabi, UAE, 1–4 November. http://dx.doi.org/10.2118/138241-MS.

Konsta-Gdoutos, M.S., Metaxa, Z.S. and Shah, S.P., 2010. Multi-scale mechanical and fracture characteristics and early-age strain capacity of high performance carbon nanotube/cement nanocomposites. Cem. Concr. Compos., 32(2): 110-115. http://dx.doi.org/10.1016/j.cemconcomp.2009.10.007.

Kovler, K. et al., 2007. Internal curing of concrete, state-of-the-art Report of RILEM Technical Committee 196-ICC. RILEM Rep., 41.

Krishnamoorti, R., 2006. Extracting the benefits of nanotechnology for the oil industry. J. Petroleum Technol., 58(11): 24-26.

Li, G.Y., Wang, P.M. and Zhao, X., 2005. Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes. Carbon, 43(6): 1239-1245. http://dx.doi.org/10.1016/j.carbon.2004.12.017.

Li, H., Xiao, H.-g., Yuan, J. and Ou, J., 2004. Microstructure of cement mortar with nano-particles. Compos. Part B: Eng., 35(2): 185-189. http://dx.doi.org/10.1016/S1359-8368(03)00052-0.

Li, H., Zhang, M.-h. and Ou, J.-p., 2006. Abrasion resistance of concrete containing nano-particles for pavement. Wear, 260(11-12): 1262-1266. http://dx.doi.org/10.1016/j.wear.2005.08.006.

Li, L. et al. 2013. Vital Role of Nanotechnology and Nanomaterials in the Field of Oilfield Chemistry. Proc., International Petroleum Technology Conference, Beijing, China, 26–28 March. http://dx.doi.org/10.2523/16401-MS.

Lindgreen, H., Geiker, M., Krøyer, H., Springer, N. and Skibsted, J., 2008. Microstructure engineering of Portland cement pastes and mortars through addition of ultrafine layer silicates. Cem. Concr. Compos., 30(8): 686-699. http://dx.doi.org/10.1016/j.cemconcomp.2008.05.003.

Liu, J. and Vipulanandan, C. 2012. Failure Modes of Oil Well Cement During Service Life. Proc., Hurricanes-2012 Conference & Exhibition.

Lura, P., Jensen, O.M. and van Breugel, K., 2003. Autogenous shrinkage in high-performance cement paste: An evaluation of basic mechanisms. Cem. Concr. Res., 33(2): 223-232. http://dx.doi.org/10.1016/S0008-8846(02)00890-6.

Maserati, G. et al. 2010. Nano-emulsions as cement spacer improve the cleaning of casing bore during cementing operations. Proc., SPE Annual Technical Conference and Exhibition, Florence, Italy, 19-22 September. http://dx.doi.org/10.2118/133033-MS.

Matteo, C., Candido, P., Vera, R.R. and Francesca, V., 2012. Current and future nanotech applications in the oil industry. Am. J. Appl. Sci., 9(6): 784-793.

McCulloch, J., Gastineau, J., Bour, D. and Ravi, K., 2003. Life Cycle Modeling of Wellbore Cement Systems Used for Enhanced Geothermal System Development. Geotherm. Resour. Counc. Transactions, 27: 147-154.

Mercado, Y.A.P., Ramirez, J.C.C., Acevedo, A.C.H. and Méndez, S.I.M., 2012. Nano-additive for hydrocarbon well cementing operations. Google Patents.

Metaxa, Z.S., Konsta-Gdoutos, M.S. and Shah, S.P. 2010. Mechanical properties and nanostructure of cement-based materials reinforced with carbon nanofibers and Polyvinyl Alcohol (PVA) microfibers. Proc., American Concrete Institute, ACI Special Publication.

Mo, L., Deng, M. and Tang, M., 2010. Effects of calcination condition on expansion property of MgO-type expansive agent used in cement-based materials. Cem. Concr. Res., 40(3): 437-446. http://dx.doi.org/10.1016/j.cemconres.2009.09.025.

Mohr, B., Premenko, L., Nanko, H. and Kurtis, K. 2005. Examination of wood-derived powders and fibers for internal curing of cement-based materials. Proc., Proceedings of the 4th Interntational Seminar: Self-Desiccation and Its Importance in Concrete Technology.

Mohr, B.J., 2005. Durability of pulp fiber-cement composites. PhD Thesis, Georgia Institute of Technology.

Moradpour, R., Taheri-Nassaj, E., Parhizkar, T. and Ghodsian, M., 2013. The effects of nanoscale expansive agents on the mechanical properties of non-shrink cement-based composites: The influence of nano-MgO addition. Compos. Part B: Eng., 55: 193-202. http://dx.doi.org/10.1016/j.compositesb.2013.06.033.

Morales, D., Gutiérrez, J.M., Garcia-Celma, M. and Solans, Y., 2003. A study of the relation between bicontinuous microemulsions and oil/water nano-emulsion formation. Langmuir, 19(18): 7196-7200. http://dx.doi.org/10.1021/la0300737.

Morris, W., Criado, M.A., Robles, J. and Bianchi, G. 2003. Design of High Toughness Cement for Effective Long Lasting Well Isolations. Proc., SPE Latin American and Caribbean Petroleum Engineering Conference, Port-of-Spain, Trinidad, West Indies, 27-30 April. http://dx.doi.org/10.2118/81001-MS.

Mukhopadhyay, A., 2011. Next-Generation Nano-based Concrete Construction Products: A Review. In: K. Gopalakrishnan, B. Birgisson, P. Taylor and N. Attoh-Okine (Editors), Nanotechnology in Civil Infrastructure. Springer Berlin Heidelberg, pp. 207-223. http://dx.doi.org/10.1007/978-3-642-16657-0_7.

Nagataki, S. and Gomi, H., 1998. Expansive admixtures (mainly ettringite). Cem. Concr. Compos., 20(2-3): 163-170. http://dx.doi.org/10.1016/S0958-9465(97)00064-4.

Nazari, A. and Riahi, S., 2011a. Al2O3 nanoparticles in concrete and different curing media. Energy Build., 43(6): 1480-1488. http://dx.doi.org/10.1016/j.enbuild.2011.02.018.

Nazari, A. and Riahi, S., 2011b. The effects of Cr2O3 nanoparticles on strength assessments and water permeability of concrete in different curing media. Mater. Sci. Eng.: A, 528(3): 1173-1182. http://dx.doi.org/10.1016/j.msea.2010.09.099.

Nazari, A. and Riahi, S., 2011c. The effects of SiO2 nanoparticles on physical and mechanical properties of high strength compacting concrete. Compos. Part B: Eng., 42(3): 570-578. http://dx.doi.org/10.1016/j.compositesb.2010.09.025.

Nazari, A. and Riahi, S., 2011d. The effects of TiO2 nanoparticles on flexural damage of self-compacting concrete. Int. J. Damage Mech., 20(7): 1049-1072. http://dx.doi.org/10.1177/1056789510385262.

Nazari, A. and Riahi, S., 2011e. The effects of zinc dioxide nanoparticles on flexural strength of self-compacting concrete. Compos. Part B: Eng., 42(2): 167-175. http://dx.doi.org/10.1016/j.compositesb.2010.09.001.

Nelson, E.B. and Guillot, D., 2006. Well Cementing. Schlumberger.

Nochaiya, T. and Chaipanich, A., 2011. Behavior of multi-walled carbon nanotubes on the porosity and microstructure of cement-based materials. Appl. Surf. Sci., 257(6): 1941-1945. http://dx.doi.org/10.1016/j.apsusc.2010.09.030.

Pacheco-Torgal, F. and Jalali, S., 2011. Nanotechnology: advantages and drawbacks in the field of construction and building materials. 25(2): 582-590.

Pacheco-Torgal, F., Miraldo, S., Ding, Y. and Labrincha, J., 2013. Targeting HPC with the help of nanoparticles: an overview. Constr. Build. Mater., 38: 365-370. http://dx.doi.org/10.1016/j.conbuildmat.2012.08.013.

Pang, X., Boul, P.J. and Cuello Jimenez, W., 2014. Nanosilicas as Accelerators in Oilwell Cementing at Low Temperatures. SPE Drill. Completion, 29(1): 98-105. http://dx.doi.org/10.2118/168037-PA.

Parveen, S., Rana, S. and Fangueiro, R., 2013. A review on nanomaterial dispersion, microstructure, and mechanical properties of carbon nanotube and nanofiber reinforced cementitious composites. J. Nanomater., 2013. http://dx.doi.org/10.1155/2013/710175.

Pedersen, R. et al. 2006. Cementing of an Offshore Disposal Well Using a Novel Sealant That Withstands Pressure and Temperature Cycles. Proc., IADC/SPE Drilling Conference, Miami, Florida, 21–23 February. http://dx.doi.org/10.2118/98891-MS.

Polat, R., Demirboğa, R. and Khushefati, W.H., 2015. Effects of nano and micro size of CaO and MgO, nano-clay and expanded perlite aggregate on the autogenous shrinkage of mortar. Constr. Build. Mater., 81: 268-275. http://dx.doi.org/10.1016/j.conbuildmat.2015.02.032.

Ponmani, S., Nagarajan, R. and Sangwai, J., 2013. Applications of Nanotechnology for Upstream Oil and Gas Industry. J. Nano Res., 24: 7-15. http://dx.doi.org/10.4028/www.scientific.net/JNanoR.24.7

Pourafshary, P. et al. 2009. Priority Assessment of Investment in Development of Nanotechnology in Upstream Petroleum Industry. Proc., SPE Saudi Arabia Section Technical Symposium and Exhibition, AlKhobar, Saudi Arabia, 09–11 May. http://dx.doi.org/10.2118/126101-MS.

Qian, S.Z., Zhou, J. and Schlangen, E., 2010. Influence of curing condition and precracking time on the self-healing behavior of Engineered Cementitious Composites. Cem. Concr. Compos., 32(9): 686-693. http://dx.doi.org/10.1016/j.cemconcomp.2010.07.015.

Ramos, X.G., Martinez, C.I., Hunter, W.J. and Ravi, K. 2009. Three Levels of Assurance Deployed for Reliable Zonal Isolation in Latin America. Proc., SPE Latin American and Caribbean Petroleum Engineering Conference, Cartagena, Colombia, 31 May–3 June. http://dx.doi.org/10.2118/121310-MS.

Ravi, K., Bosma, M. and Gastebled, O. 2002. Improve the Economics of Oil and Gas Wells by Reducing the Risk of Cement Failure. Proc., IADC/SPE Drilling Conference, Dallas, Texas, 26–28 February. http://dx.doi.org/10.2118/74497-MS.

Reddy, B.R., Xu, Y., Ravi, K., Gray, D. and Pattillo, P.D., 2009. Cement-shrinkage measurement in oilwell cementing - A comparative study of laboratory methods and procedures. SPE Drill. Completion, 24(1): 104-114. http://dx.doi.org/10.2118/103610-MS.

Roddy, C.W. et al., 2010. Cement compositions comprising latex and a nano-particle and associated methods. Google Patents.

Roddy, C.W., Covington, R.L., Chatterji, J. and Brenneis, D.C., 2013. Cement compositions and methods utilizing nano-clay. Google Patents.

Rongbing, B. and Jian, S., 2005. Synthesis and evaluation of shrinkage-reducing admixture for cementitious materials. Cem. Concr. Res., 35(3): 445-448. http://dx.doi.org/10.1016/j.cemconres.2004.07.009.

Roy-Delage, S.L., Baumgarte, C., Thiercelin, M. and Vidick, B. 2000. New Cement Systems for Durable Zonal Isolation. Proc., IADC/SPE Drilling Conference, New Orleans, Louisiana, 23–25 February. http://dx.doi.org/10.2118/59132-MS.

Roy-Delage, S.L. and James, S., 2008. Flexible cementing compositions and methods for high-temperature wells. Google Patents.

Roy-Delage, S.L. and Thiercelin, M., 2004. Cementing compositions and applications of such compositions for cementing oil wells or the like. Google Patents.

Sadrmomtazi, A. and Fasihi, A., 2012. The Role of Nano-SiO2 Addition in the Mechanical Properties of RHA Composite Cement Mortars. Adv. Mater. Res., 346: 18-25. http://dx.doi.org/10.4028/www.scientific.net/AMR.346.18.

Saint-Marc, J., Garnier, A. and Bois, A.P. 2008. Initial State of Stress: The Key to Achieving Long-Term Cement-Sheath Integrity. Proc., SPE Annual Technical Conference and Exhibition, Denver, Colorado, USA, 21–24 September. http://dx.doi.org/10.2118/116651-MS.

Saliba, J., Rozière, E., Grondin, F. and Loukili, A., 2011. Influence of shrinkage-reducing admixtures on plastic and long-term shrinkage. Cem. Concr. Compos., 33(2): 209-217. http://dx.doi.org/10.1016/j.cemconcomp.2010.10.006.

Sanchez, F. and Ince, C., 2009. Microstructure and macroscopic properties of hybrid carbon nanofiber/silica fume cement composites. Compos. Sci. Technol., 69(7-8): 1310-1318. http://dx.doi.org/10.1016/j.compscitech.2009.03.006.

Sanchez, F. and Sobolev, K., 2010. Nanotechnology in concrete – A review. Constr. Build. Mater., 24(11): 2060-2071. http://dx.doi.org/10.1016/j.conbuildmat.2010.03.014.

Sant, G. et al., 2011. The origin of early age expansions induced in cementitious materials containing shrinkage reducing admixtures. Cem. Concr. Res., 41(3): 218-229. http://dx.doi.org/10.1016/j.cemconres.2010.12.004.

Santra, A., Boul, P.J. and Pang, X. 2012. Influence of nanomaterials in oilwell cernent hydration and mechanical properties. Proc., SPE International Oilfield Nanotechnology Conference and Exhibition, Noordwijk, The Netherlands, 12-14 June. http://dx.doi.org/10.2118/156937-MS.

Shadravan, A., Schubert, J., Amani, M. and Teodoriu, C. 2014. HPHT Cement Sheath Integrity Evaluation Method for Unconventional Wells. Proc., SPE International Conference on Health, Safety, and Environment, Long Beach, California, USA, 17–19 March. http://dx.doi.org/10.2118/168321-MS.

Stefanidou, M. and Papayianni, I., 2012. Influence of nano-SiO2 on the Portland cement pastes. Compos. Part B: Eng., 43(6): 2706-2710. http://dx.doi.org/10.1016/j.compositesb.2011.12.015.

Stiles, D. and Hollies, D. 2002. Implementation of Advanced Cementing Techniques to Improve Long Term Zonal Isolation in Steam Assisted Gravity Drainage Wells. Proc., SPE International Thermal Operations and Heavy Oil Symposium and International Horizontal Well Technology Conference, Calgary, Alberta, Canada, 4–7 November. http://dx.doi.org/10.2118/78950-MS.

Sukontasukkul, P. and Chaikaew, C., 2006. Properties of concrete pedestrian block mixed with crumb rubber. Constr. Build. Mater., 20(7): 450-457. http://dx.doi.org/10.1016/j.conbuildmat.2005.01.040.

Tang, L.C. et al., 2013. Mechanical properties and fracture behaviors of epoxy composites with multi-scale rubber particles. Mater. Chem. Phys., 141(1): 333-342. http://dx.doi.org/10.1016/j.matchemphys.2013.05.018.

Teodoriu, C., Kosinowski, C., Amani, M., Schubert, J. and Shadravan, A., 2013. Wellbore Integrity and Cement Failure at HPHT Conditions. Int. J. Eng., 2(2): 2305-8269.

Thiercelin, M.J., Dargaud, B., Baret, J.F. and Rodriquez, W.J., 1998. Cement Design Based on Cement Mechanical Response. SPE Drill. Completion, 13(4): 266-273. http://dx.doi.org/10.2118/52890-PA.

Thomas, R. et al., 2008. Miscibility, morphology, thermal, and mechanical properties of a DGEBA based epoxy resin toughened with a liquid rubber. Polym., 49(1): 278-294. http://dx.doi.org/10.1016/j.polymer.2007.11.030.

Tyson, B.M., Abu Al-Rub, R.K., Yazdanbakhsh, A. and Grasley, Z., 2011. Carbon nanotubes and carbon nanofibers for enhancing the mechanical properties of nanocomposite cementitious materials. J. Mater. Civ. Eng., 23(7): 1028-1035. http://dx.doi.org/10.1061/(ASCE)MT.1943-5533.0000266.

Van Tittelboom, K. and De Belie, N., 2013. Self-healing in cementitious materials—A review. Mater., 6(6): 2182-2217. http://dx.doi.org/10.3390/ma6062182.

Weiss, J., Lura, P., Rajabipour, F. and Sant, G., 2008. Performance of shrinkage-reducing admixtures at different humidities and at early ages. ACI Mater. J., 105(5).

Williams, R.H. et al. 2011. Flexible, Expanding Cement System (FECS) Successfully Provides Zonal Isolation Across Marcellus Shale Gas Trends. Proc., Canadian Unconventional Resources Conference, Calgary, Alberta, Canada, 15–17 November. http://dx.doi.org/10.2118/149440-MS.

Yang, Z., Liu, J., Liu, J., Li, C. and Zhou, H., 2011. Silica modified PP fiber for improving crack-resistance of cementitious composites. Adv. Mater. Res., 332-334: 2058-2064. http://dx.doi.org/10.4028/www.scientific.net/AMR.332-334.2058.

Yao, X. and Hua, S. 2007. Design of Novel Composite Agent for Improving the Toughness of Oil-Well Cement Sheath. Proc., SPE International Symposium on Oilfield Chemistry, 28 February–2 March. http://dx.doi.org/10.2118/106010-MS.

Zargartalebi, M., Kharrat, R. and Barati, N., 2015. Enhancement of surfactant flooding performance by the use of silica nanoparticles. Fuel, 143: 21-27. http://dx.doi.org/10.1016/j.fuel.2014.11.040.

Zhang, T. et al. 2011. Engineered Nanoparticles as Harsh-Condition Emulsion and Foam Stabilizers and as Novel Sensors. Proc., Offshore Technology Conference, Houston, Texas, USA, 2–5 May. http://dx.doi.org/10.4043/21212-MS.