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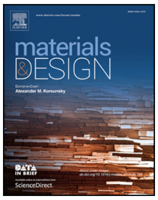

Influence of olivine nano-silica on hydration and performance of oil-well cement slurries

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ABSTRACT

This research provides an explorative study to determine the influence of a newly developed nano-silica obtained from the dissolution of olivine (OnS) as an additive in cementitious slurries for oil and gas wells. In this context, the heat evolution of normal density slurries of Class G oil-well cement and OnS, cured at different temperatures and atmospheric pressure, is examined by isothermal calorimetry. Under isothermal and isobaric conditions, the dependency of cement hydration kinetics on curing temperature is related to the activation energy and the degree of hydration of the cementing slurries. The apparent activation energy of the different slurries with OnS is estimated using static and dynamic methods. In addition, the effect of adding OnS in conventional density slurries is investigated using standard methods and procedures such as thickening time, rheology, settling and ultrasonic compressive strength determination, all prescribed by corresponding API standards. A beneficial effect of the OnS addition is found on stability, rheology and hydration degree of cementing slurries. Finally, the potential use of olivine nano-silica as an accelerator and enhancer of mechanical properties of oil-well cementitious composites is demonstrated.

1. Introduction

Cementing operations in oil and gas well consists of pumping a cement slurry down the casing and back up the annular space where it is allowed to set forming a protective sheath and providing zonal isolation. The objective is to prevent contamination between formations such as oil or gas entering ground waters or, water or gas entering oil producing zones in the well. Without complete isolation in the wellbore, the well may never reach its full production potential [1]. Research in recent years has focused on the use of materials that can provide high performance to enhance the useful lifetime of the well and reduce costs associated with their repair or losses due to failures in the cement sheath. One such material is amorphous silica either in the form of micro-silica or nano-silica.

Micro-silica (mS), originally used in oil-well cementing operations by Grinrod et al. [2], to prevent annular gas migration has since been shown to also enhance rheological properties, slurry stability, compressive strength development, and fluid loss control. Drawbacks to the use of mS in some operations are its bulk handling in offshore operations, namely high storage volumes and the potential for solids settling when used as a mS suspension. Colloidal nano-silica was found to resolve the drawbacks of mS in overcoming the solids settling and in addition decreased storage volumes as less material was required to accomplish the same desired results due to its extended surface area (between 50 to 500 m^2/g) [3]. Additional applications of colloidal nano-silica have been lightweight cementing, low-rheology cementing, horizontal well cementing and annular gas control. Several researchers [4–7] have demonstrated the benefits of using colloidal nano-silica, combined with optimized designs, to produce efficient cementing systems. In these studies it is stated that nano-silica enhances the early and final strength, decreases the final permeability of the hardened cement sheath, allows better control of the free fluid, decreases the fluid-loss and also increases the static gel strength. In addition, it was demonstrated [7] that colloidal nano-silica can be used as a chloride free accelerator for low temperature applications and as an ultra-fine filler in conventional, squeezable and optimized packing volume fraction (PVF) cementing slurries [7–10]. Although nano-silica additions have shown beneficial effects there are still questions as to its reaction mechanism and how it impacts on long-term hydration [11–15]. Bjönström et al. [11], for example, queried whether the accelerated hydration on addition of nano-silica was due to either its high surface activity or to chemical (pozzolanic) reaction upon dissolution. Byung-Wan et al. [12] found that at higher nano-silica content, adjustments in water and dispersant contents were required to not only maintain mixability and rheological properties but also to prevent excessive

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self-desiccation and cracking. Shi et al. [13], reported that compressive strength increased as the content of nano-silica was increased up to an optimum value, whereby further increase in nano-silica content notably decreased the compressive strength. According to other researchers [14, 15] if nano-silica particles are not well dispersed within the cement slurry, due possibly to high content of nano-silica or improper dispersion techniques, they tend to form agglomerates or clusters that can create weak zones within the matrix leading to low strength and high porosity.

Nano-silica technology, offers a means to obtain substantial changes in the chemical, physical and mechanical properties at the macroscale, resulting from the unique physical and chemical properties of the nano-silica materials due to their nanometric size. Currently, nano-silica is produced commercially either by neutralization of sodium silicate solutions with acid (this material is referred to as colloidal silica) or flame hydrolysis (pyrogenic silica) [16]. These production methods involve steps with temperatures above 1000 °C [16–18] that involves large amount of fuel consumption making these processes: a) expensive due to the price of fuel, b) environmentally unfriendly due to high CO_2 emissions, and c) unsustainable as a result of increasing scarcity of fuels. A newly developed alternative method for obtaining nano-silica having low energy requirements has been reported [16, 17]. This method involves the dissolution of one of the fastest weathering silicate minerals, olivine, in acid at low temperature (between 50 and 90 °C) to produce an amorphous nano-silica of high quality [17, 19]. Furthermore, in the production of OnS it is possible to use waste acids as reported by [16].

Published results [18] on hydration of ordinary Portland cement with addition of olivine nano-silica (OnS) accelerated the setting time while heat of hydration remained constant. In addition rheological studies showed, with OnS, an increase in yield point, viscosity and gel strength.

As established by [16] the OnS has different characteristics compared to colloidal and pyrogenic nano-silica. OnS is produced at negative pH leading to formation of agglomerated silica nano-particles with higher specific surface area (200–400 m^2/g) and greater concentration of silanol (OH) surface groups that impact its reactivity. Furthermore, the nano-silica produced in the OnS method has a morphology of a 3D network of small silica particles of interconnected beads. The aim of this study is to understand how the different characteristics of OnS affect the hydration kinetics (heat of hydration and activation energy) and the physical properties of Class G cement slurries for oil and gas well applications. Calorimetric methods were used in conjunction with standard methods and procedures as described by corresponding American Petroleum Institute (API) standards [20, 21]. In calorimetric analyses, slurries with standard oil-well mS were used as a reference additive material as the current source of amorphous silica in well cementing operations. Slurries for testing with standard methods and procedures were based on laboratory designs for field application.

2. Materials and experimental methods

2.1. Materials

In this study the oil-well cement used was supplied by Dyckerhoff (Germany) and was classified as Class G, according to API 10A [20] specification, with mineralogical composition (wt%) C_3S (alite) – 64.00, C_2S (belite) – 11.92, C_3A (celite) – 1.20, C_4AF (ferrite) – 14.2 and ($C_4AF + 2C_3A$) (aluminates) – 16.6 based on Bogue calculation as provided by manufacturer. A 10 wt% solids OnS dispersion [18] prepared from a synthesized pilot plant batch (15 kg) of OnS cake (Geochem Research B.V., The Netherlands) was used for calorimetric studies whereas the OnS cake (20 wt% solids) was used for conventional oil-well slurries (laboratory designed for field application) experimental testing. The OnS particles had an equivalent SiO_2 content of 99.1 wt%, density of 2.07 g/cm^3 and BET specific surface area of 399 m^2/g. An oil-well grade mS (Microlite®-P) with a 94.0 wt% of SiO_2, density of 2.3 g/cm^3 and BET specific surface area of 19 m^2/g provided by Elkem Materials (Norway) was used for comparison with the OnS in calorimetric studies. In addition, a commercial dispersant based on a modified polycarboxylate ether, PCE-type, supplied by BASF (Germany) was used to provide dispersed slurries for the calorimetric study. Additional additives, oil-well grade dispersant polynaphthalene sulfonate, PNS-type, antifoam long-chain hydroxyl compound and anti-settling biopolymer used for determining the influence of OnS on conventional oil-well slurries were provided by Total E&P (France). Distilled water was used in all experiments.

2.2. Experimental methods

2.2.1. Calorimetric studies

A total of eight standard cement slurries (CS) having a density of 1.89 g/cm^3 were prepared according to the compositions shown in Table 1. Initially, the water, PCE-type dispersant and the OnS or powder mS were mixed at 20 s intervals, in a high energy (600 W) hand blender (Philips HR1363). Thereafter the cement was added in 15 s and the mixing was continued for 1 min. A 10 g sample of the cement slurry was then poured into a glass ampoule (20 mL) that was then placed into the calorimeter chamber of an 8-channel TAM® Air isothermal micro calorimeter from TA Instruments (U.S.A.). All the slurries were tested twofold for 48 h and at different temperatures (20, 40 and 60 °C). The results were analyzed using the TAM assistance software to determine, the induction period, slope of the acceleration period (SAP), relative setting time (RST) and time to reach the maximum hydration peak (TMHP) as proposed by Bensted [22, 23] and Wadsö [24].

2.2.2. Degree of hydration (α) and activation energy (Ea)

The progress of the hydration of the cement slurries was quantified by the hydration degree (α), which varies from 0 to 1. For this study, the hydration degree is estimated according to [25] as the ratio of heat evolved at time t to the total amount of heat available (Q_{max}). The value Q_{max} was calculated according to [26] using the cement composition and amount and type of silica. The maximum heat of OnS or mS was assumed to be equal from the amount of amorphous SiO_2 in both silica types (780 J/g according to [25]). The activation energy (Ea) was estimated using two different methods. The first method applied and by far the most widely used [26] considered a first order reaction rate (Arrhenius-type) expression as follows:

$$k = A \cdot e^{\frac{-Ea}{RT}} \tag{4}$$

where R equals the natural gas constant (8.314 J/mol/K), T equals the temperature in K at which reaction occurs, k equals the rate of heat flow evolution (dH/dt), A equals the proportionality constant, and Ea equals the activation energy (J/mol). In the present study, k was calculated from the heat flow curves obtained for each slurry tested. It is derived as the slope of the best linear fit during the acceleration period. To quantify the apparent Ea, the methodology described by [27] was applied. The second method applied to determine the activation energy was the incremental reaction rate method. This method considers that the reaction rate is a function of the hydration degree (considering a differential first order rate approximation) [26]. The reaction rate is calculated incrementally at each point where heat flow evolution was measured at a constant hydration degree. Thus, the activation energy is calculated from the heat rate results according to [28] as follows:

$$Ea(\alpha) = R\left[\frac{T_1 \cdot T_2}{T_1 - T_2} \cdot \ln\left(\frac{\frac{d\alpha_1}{dt}}{\frac{d\alpha_2}{dt}}\right)\right] \tag{5}$$

Table 1
Standard slurry composition used for hydration kinetic studies (density 1.89 g/cm^3).

Materials	Ref-1	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
OnS (% bwoc)[a]	0	0.5	1.0	1.5	2.0	0	0	0
mS (% bwoc)	0	0	0	0	0	1.0	2.0	10.0
Class G (%)	100	100	100	100	100	100	100	100
Water (% bwoc)	44	44.1	44.3	44.4	44.6	43.7	43.5	41.3
PCE-type (L/100 kg)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
w/b	0.44	0.44	0.44	0.44	0.45	0.44	0.44	0.41

CS: cement slurry.
[a] Equivalent SiO_2 content.

in which R equals the natural gas constant, T_1 and T_2 are the curing temperatures (in K) and $d\alpha_1/dt$, $d\alpha_2/dt$ are the rate of hydration at T_1 and T_2, respectively. For the calculation of the activation energy using the incremental reaction rate method the data at 20 to 60 °C was considered.

2.2.3. Performance tests of conventional oil-well slurries with OnS

Three oil-well cement slurry compositions (Table 2) with a standard density of 1.90 g/cm^3 were used for this study. The first composition, Ref-2, was optimized by adjusting the amount of additives to obtain an easy to mix slurry with low rheological parameters and good stability. Two concentrations of OnS cake were used, 0.5 and 5.0% based on the weight of cement (bwoc), in order to observe the variations in performance of such compositions. All slurries were prepared as per API RP 10B-2 [21] with the modification that anti-settling additive was first added to the mix water and allowed to hydrate for 5 min under gentle agitation, then the antifoam and OnS cake were added followed by the PNS-type dispersant. Cement Class G was then added within 15 s at 4000 ± 100 rpm and then mixed for 35 s at 12,000 ± 250 rpm. All slurries were mixable, pourable and without evidence of settling. Density, rheology, free-fluid and sedimentation, thickening time and compressive strength data for the slurries were carried out according to procedures given in API RP 10B-2 [21].

Thickening-time (TT) is a measure of the length of time a cement slurry remains pumpable. TT was recorded as the time between the first application of temperature and pressure to the pressurized consistometer and the time at which a consistency of 100 Bearden units (Bc) was reached. Bearden unit of consistency or Bc is the measure of the consistency of a cement slurry with no direct conversion factor to more common units of viscosity [1]. Time to reach consistency values of 30, 40, 70 and 100 Bc were reported.

3. Results and discussion

3.1. Calorimetric studies

Fig. 1 shows the resulting plots for the heat flow (Fig. 1a, b and c) and total heat curves (Fig. 1d, e and f) as a function of elapsed time for cement slurries tested at 20, 40 and 60 °C, respectively. It is clear from Fig. 1 that, with increasing temperature, the maximum hydration peak increases, while the time to reach the peak decreases. This means, that the rate of cement hydration is accelerated with temperature, consistent with the laws of chemical kinetics. Additionally, it is observed that the peak width decreases with increasing temperature, indicating a faster hydration rate with time. This is associated with the particular mechanism of cement hydration as the hydration rate depends on the total degree of reaction [7]. It can also be observed in Fig. 1d–f that the accumulated total heat increases with temperature. These observations are valid for all the cement slurries tested.

Table 2
Conventional slurry compositions used for the performance based tests (density 1.90 g/cm^3).

Materials	Ref-2	CS-8	CS-9
OnS cake (% bwoc)[a]	0	0.5	5.0
Class G (%)	100	100	100
Water (% bwoc)	44.0	43.6	40.0
PNS-type (L/100 kg)	0.092	0.092	0.092
Antifoam (L/100 kg)	0.075	0.075	0.075
Anti-settling (% bwoc)	0.15	0.15	0.15
w/b	0.44	0.44	0.44

CS: cement slurry.
[a] OnS cake with 20 wt% solids.

At 20 °C, Fig. 1a, standard slurries with 1.0 and 2.0% bwoc mS did not affect the induction period (defined in Fig. 1a) or the maximum peak whereas at 10% bwoc mS the induction period is shortened and the maximum peak increased. Table 3, provides additional data and illustrates again the difference at 10% bwoc mS in terms of RST, TMHP and SAP values. It is of note that equivalent results can be obtained using 1.0% OnS instead of 10% bwoc mS. Santra et al. [7] reported similar results for a Class H cement with a density of 1.78 g/cm^3 (14.86 lbm/gal) where 0.45% bwoc nano-silica (average particle size of 30 nm) give similar calorimetric curves as 10% bwoc mS.

At 40 °C, Fig. 1b, 1.0 and 2.0% bwoc mS additions increased the induction period whereas 10% bwoc mS showed no effect. The RST were however shortened on addition of 2.0 and 10% bwoc mS while the SAP at 2.0% was increased (Table 4). Trends at 60 °C are similar to those at 40 °C (Table 5), one notable difference was a shoulder observed at longer hydration times with the 10% bwoc mS addition, Fig. 1c inset. This peak can be attributed to an accelerated pozzolanic reaction [18] and may also explain the maximum total heat plateau occurring faster than in other samples, Fig. 1f. In other words, the higher hydration degree induced at early age it is probably due to the filler effects, consequently, more hydration products (C-S-H and portlandite) is precipitated. This provides more portlandite to react with mS generating additional heat of hydration. This pozzolanic reaction allows the 10% mS slurry to reach its maximum total heat plateau faster than the other test samples. However, the final total heat is similar to the reference slurry at 48 h. Comparing the results obtained with mS to that obtained with OnS several observations can be made. At 20 °C, Fig. 1a, it is possible to observe that the height of the peak slightly increases with the addition of OnS and the induction period almost linearly decreases with higher additions of OnS (Table 3). However the most notable difference is the separation of the peak with a distinct shoulder occurring before the maximum peak at 1.0 and 2.0% OnS. In this case it is assumed that the shoulder is related to hydration of the silicate phases ($C_2S + C_3S$) hydration and the maximum peak to the aluminates ($C_3A + C_4AF$) hydration. The acceleration of the aluminate phases also produces a widening of the main hydration peak, which is mainly caused by the so-called filler effect [29] and the acceleration of the hydration due to an enhanced nucleation. This nucleation effect has been reported by different researchers on other amorphous nano-silica particles using SEM analysis [14, 15, 30].

Table 3 shows in more detail the effects of OnS and mS on the hydration kinetics of the cementing slurries tested. In this table, it is possible to observe that the RST and TMHP for slurries with OnS addition are shorter (1 to 7 h less). Furthermore, it is possible to confirm that the hydration rate (SAP) increases with the addition of OnS. At this

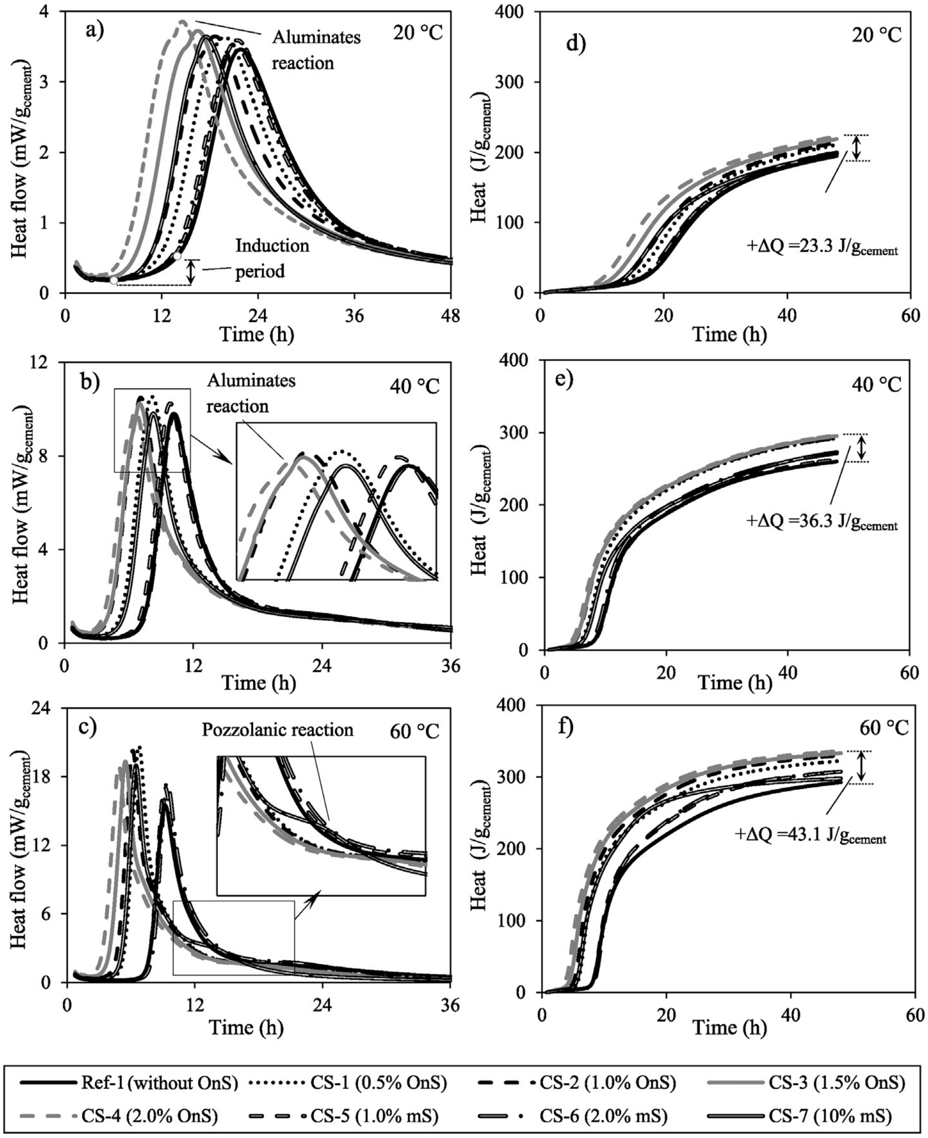

Fig. 1. Heat flow a) 20 °C, b) 40 °C and c) 60 °C and total heat d) 20 °C, e) 40 °C and f) 60 °C curves for standard density slurries (1.89 g/cm^3).

temperature, equivalent results can be obtained with 1.0% of OnS as with 10% bwoc of mS. The results and general trends observed at 40 °C are only slightly different to those at 20 °C. It is notable at 40 °C, that the aluminates peak is present at all concentrations of OnS studied, being more evident at higher OnS concentrations, Fig. 1b. Differences in reactivity between OnS and mS are evident from the TMHP time and the SAP obtained, Table 4. It appears that SAP initially increases with the addition of OnS, but decreases for concentrations of 1.5–2.0%, though it is possible this is a consequence of error considering a unique reaction rate for all cement phases during the measurement of the SAP. The

Table 3
Parameters of the hydration kinetics of standard cement slurries (normal density 1.89 g/cm^3) tested at 20 °C.

Slurry	Induction period (h:min)	RST (h:min)	TMHP (h:min)	SAP (mW/gh)
Ref-1	9:17	4:31	21:32	0.553
CS-1 (0.5% OnS)	8:30	2:52	19:39	0.598
CS-2 (1.0% OnS)	4:59	3:55	18:28*	0.650
CS-3 (1.5% OnS)	4:19	3:15	16:20*	0.693
CS-4 (2.0% OnS)	2:41	3:22	14:32*	0.744
CS-5 (1.0% mS)	9:15	4:39	21:22	0.574
CS-6 (2.0% mS)	9:02	4:11	21:01	0.561
CS-7(10% mS)	6:26	3:07	17:25*	0.691

RST: relative setting time, TMHP: time to reach the maximum hydration peak, SAP: slope acceleration period, (*) aluminates reaction peak. All percentages are based on the weight of cement (bwoc).

Table 4
Parameters of the hydration kinetics of standard cement slurries (density 1.89 g/cm^3) tested at 40 °C.

Slurry	Induction period (h:min)	RST (h:min)	TMHP (h:min)	SAP (mW/gh)
Ref-1	2:38	2:13	10:08	4.424
CS-1 (0.5% OnS)	1:56	1:36	8:03*	4.712
CS-2 (1.0% OnS)	1:33	1:21	7:08*	4.782
CS-3 (1.5% OnS)	1:17	1:27	7:00*	4.619
CS-4 (2.0% OnS)	1:43	1:28	6:34*	4.580
CS-5 (1.0% mS)	3:50	2:11	10:16	4.401
CS-6 (2.0% mS)	3:58	1:37	9:51	4.637
CS-7(10% mS)	2:38	1:44	8:17	4.490

RST: relative setting time, TMHP: time to reach the maximum hydration peak, SAP: slope acceleration period, (*) aluminates reaction peak. All percentages are based on the weight of cement (bwoc).

Table 5
Parameters of the hydration kinetics of standard cement slurries (density 1.89 g/cm^3) tested at 60 °C.

Slurry	Induction period (h:min)	RST (h:min)	TMHP (h:min)	SAP (mW/gh)
Ref-1	2:56	0:47	9:13	12.470
CS-1 (0.5% OnS)	2:03	0:50	6:46	17.181
CS-2 (1.0% OnS)	2:00	0:55	6:07	15.600
CS-3 (1.5% OnS)	1:39	0:53	5:28	14.047
CS-4 (2.0% OnS)	1:22	1:04	4:50	13.600
CS-5 (1.0% mS)	3:28	0:53	9:11	14.285
CS-6 (2.0% mS)	3:06	0:57	9:23	15.210
CS-7(10% mS)	1:45	0:43	6:27	16.223

RST: relative setting time, TMHP: time to reach the maximum hydration peak, SAP: slope acceleration period. All percentages are based on the weight of cement (bwoc).

Table 7
Estimated average activation energy (Ea) of cement slurries (density 1.89 g/cm^3).

Slurry	Slope method (static)	Incremental method (dynamic)	Incremental method (dynamic)
	$Ea_{20-40-60}$ (kJ/mol)	Ea_{20-40} (kJ/mol)	Ea_{40-60} (kJ/mol)
Ref-1	63.57	38.18 ± 0.09 (39.57)	43.34 ± 0.05 (43.49)
CS-1	67.86	38.12 ± 0.11 (38.99)	43.37 ± 0.14 (41.40)
CS-2	64.52	38.20 ± 0.15 (39.24)	43.33 ± 0.06 (39.72)
CS-3	60.84	38.16 ± 0.05 (39.96)	43.35 ± 0.10 (40.48)
CS-4	58.34	38.14 ± 0.06 (37.89)	43.33 ± 0.07 (38.76)
CS-5	64.88	38.17 ± 0.11 (39.52)	43.29 ± 0.11 (41.92)
CS-6	67.65	38.14 ± 0.05 (38.41)	43.36 ± 0.04 (46.67)
CS-7	63.57	38.14 ± 0.07 (35.26)	43.32 ± 0.07 (43.40)

total heat obtained at 40 °C confirms also the higher reactivity of OnS compared to mS. Overall data indicates equivalent results can be obtained with 0.5% OnS compared to 10% bwoc of mS.

At 60 °C, all reaction rates are enhanced as is evident from the results shown in Fig. 1c and Table 5. Hydration peaks obtained with OnS appear slightly higher than those with mS and both are significantly higher than the reference containing no nano- or micro-silica.

The heat flow and the total heat obtained at all temperatures confirms the higher reactivity of OnS compared to mS. It is evident that OnS gives higher total heat at all concentrations compared to mS. Furthermore, OnS clearly affects at the same time the hydration of alite (C_3S), belite (C_2S) and aluminate phases ($C_3A + C_4AF$) when higher concentrations are used (>1.0% bwoc). On the contrary, concentrations of mS of 1.0 and 2.0% bwoc do not affect the maximum peak and the induction period significantly. The effect of mS is mainly noticeable for a concentration of 10% bwoc, where the induction period is shortened and the maximum peaks increased. Similar results were reported by Santra et al. [7] for oil-well cement Class H slurries with a density of 1.78 g/cm^3.

On the basis of the data it is evident that the total heat and rate of hydration of Class G oil cements could be consistently increased with incremental amounts of OnS up to 2% bwoc. It is expected that higher additions would promote inclusive higher hydration rates. For example, in [18] it is reported that the hydration rate and the extrapolated maximum heat of OPC cement with w/c of 0.5 and fixed amount of SP (0.6%) are linearly incremented with additions of OnS up to 10% bwoc.

3.2. Degree of hydration (α) and activation energy (Ea)

From the heat flow curves (Fig. 1a) the hydration degree (α) of the different cement slurries studied was calculated. The final estimated α of 10% mS slurry is the lowest in the tested range of temperatures (20 to 60 °C), Table 6, and is probably caused by the lower w/b ratio (0.41) compared to the others slurries tested (w/b = 0.44). The higher hydration degree obtained at all tested temperatures with OnS confirms again the acceleration effect. In general, the higher the temperature the greater the hydration degree of OnS slurries. Table 6 summarizes the calculated hydration degrees at 12, 24 and 48 h, for all the cement slurries tested. The data show again that a small addition of OnS (0.5% bwoc) has the same effect as 10% bwoc of micro-silica. Higher α after 12 h results in cost reductions due to the decrease in waiting time to continue the drilling operations due to cementing operations. For example, according to the specialized oil field portal www.rigzone.com [31] the average day rate for one offshore rig (medium size Jackup) is around 166,000.00 USD, this means that for each hour saved due to the decrease in waiting time of cement, the use of OnS would decrease the cost by 6,916.00 USD or 4.17%. Furthermore, operations performed can be easier due to the fact there is no need for additional blending steps of a high percentage of micro-silica.

In cement hydration, multiple reactions take place simultaneously, all of which are affected by temperature. The term apparent activation energy (Ea) is used to represent the average effect of temperature on the combined reactions. The estimated apparent activation energy results obtained for the first method (slope or linear approximation) and the second method (incremental calculation) are summarized in Table 7. It is evident from the data presented in Table 7 that the *Ea* obtained by the slope method is different for all slurries. In the case of the OnS slurries, the *Ea* increases for 0.5 and 1.0% bwoc OnS slurries (CS-1 and CS-2) compared to the reference, after that the *Ea* drops to a minimum of 58.34 kJ/mol for 2.0% OnS (CS-4). Similar observation, but with lower extent, was made for the slurries with micro-silica (mS). Different interpretations can be made based on the results. First, the drop in the activation energy, in general, confirms the acceleration effect induced by nano-silica particles.

Lower *Ea* means that the hydration reaction is enhanced. Also, according to [32], reactions with high *Ea* are very temperature-sensitive. On the contrary, reactions with low *Ea* are relatively temperature-sensitive. Based on this, the addition of OnS and mS in concentrations lower than 2.0% bwoc make the hydration reaction of Class G more temperature-sensitive. The increase in the activation energy for small amounts of OnS and mS is not expected considering the observed acceleration effects. One explanation for this is changes induced by the presence of nano-particles on the stoichiometry, kinetics and mechanism of cement hydration reaction [32]. Cement is composed of alite, belite and aluminate phases that react at different rates, so it is possible that the *Ea* may vary considerably as with the hydration degree [26].

Table 6
Estimated hydration degree (α) for the different cement slurries (density 1.89 g/cm^3) tested at 20, 40 and 60 °C, respectively.

Slurry	20 °C			40 °C			60 °C		
	α (12 h)	α (24 h)	α (48 h)	α (12 h)	α (24 h)	α (48 h)	α (12 h)	α (24 h)	α (48 h)
Ref-1	0.023	0.22	0.44	0.27	0.47	0.59	0.35	0.55	0.65
CS-1	0.026	0.28	0.48	0.37	0.54	0.66	0.48	0.64	0.73
CS-2	0.031	0.30	0.49	0.39	0.54	0.66	0.51	0.67	0.75
CS-3	0.053	0.33	0.50	0.39	0.55	0.67	0.53	0.68	0.76
CS-4	0.089	0.35	0.50	0.39	0.55	0.67	0.54	0.68	0.76
CS-5	0.023	0.23	0.45	0.26	0.47	0.49	0.37	0.59	0.70
CS-6	0.022	0.23	0.45	0.29	0.49	0.61	0.36	0.59	0.69
CS-7	0.028	0.27	0.42	0.30	0.45	0.58	0.43	0.59	0.63

Furthermore, hydration is initially reaction-rate-limited and becomes diffusion-limited as solid hydration products are formed [33]. For that reason an incremental calculation method was also applied to highlight how *Ea* is influenced by the progress of hydration (Table 7). The average *Ea* for slurries with OnS is not affected, statistically, compared to the reference slurry. Nevertheless, considering the instantaneous *Ea* calculated at very early age ($\alpha = 0.01$) which is represented by the values in parenthesis in Table 7, it is possible to observe that the *Ea* is lower than the reference. This confirms again the role of OnS to decrease the *Ea* and thus, accelerating the slurry's setting. The same observation is valid for mS slurries which also decrease *Ea*. In Table 7 it is also possible to observe that the apparent activation energy varies with the temperature ($Ea_{20-40} < Ea_{40-60}$). According to [28] this variation is not illogical insofar as the Arrhenius relation has been established for simple reactions only. This energy represents a constant with chemical significance. In the case of the reaction of cement hydration, it concerns a macroscopic apparent activation energy, which translates to no chemical law at the microscopic level [26]. Further studies [26, 34, 35] attributed the change of *Ea* with the temperature rise. The fast initial hydration caused by a high temperature leads to the formation of a thicker and more compacted layer coating of hydrated product (changes in microstructure level) around the cement grains that affects the hydration (increasing *Ea*). Variation of *Ea* with temperature was already reported by [36] for different oilwell cements (Class A, C, G and H). These researchers found, at a temperature range similar to this research (25 to 60 °C), that *Ea* increases for Class A cement from 38.4 (Ea_{25-40}) to 46.2 kJ/mol (Ea_{40-60}). On the contrary, they found that *Ea* for Class G cement decreases rather than increases with temperature, changing from 44.7 (Ea_{25-40}) to 38.5 kJ/mol (Ea_{40-60}). Despite of the differences in the activation energy between the reported research and our actual findings, the values estimated are in the same order of magnitude (38 to 43 kJ/mol) for the same class of cement (Class G). The discrepancy can be related with the use of dispersant (SP PCE-type), the type of calorimeter used and the mixing method employed (API-type warring blender vs. high energy hand mixer).

The two methods presented for the calculation of *Ea* account for the effect of temperature on the overall rate of hydration of cementitious materials. Each method has advantages and disadvantages. The linear method or Arrhenius equation is relatively straight forward, and is quite intuitive. In general, the maximum reaction rate is easy to identify when the specimens are cured at high temperatures as a clearly discernable peak signifies the end of the acceleration period. Nevertheless, according to Poole at al. [26], the method could be highly subjective at low curing temperatures and multiple activation energy values for certain mixtures could be obtained as demonstrated in the present research. The subjectivity of this method limits the conclusions that may be drawn about the temperature sensitivity of the Class G cement mixture, as well as the accuracy of any prediction. In addition, only data from the acceleration period is used to characterize the maximum rate of hydration. On the contrary, the incremental method proposed by Kada-Benameur et al. [28] appears to be the most accurate over the duration of an isothermal calorimetry test as was also established by [26]. This method provides a tool for the researcher to draw conclusions about the temperature sensitivity of different stages of cement hydration (Ea calculated up $\alpha = 0.5$). Even though, research of this area is useful for study of fundamental reaction mechanism of cementitious materials, it is recommended supplementary testing in addition to calorimetry to be accurate.

Table 8
Rheological properties of conventional slurries (density 1.90 g/cm^3).

Property	Ref-2	CS-8	CS-9	Ref-2 (AC)	CS-8 (AC)
Plastic viscosity (mPa·s)[a]	28	29	37	33	29
Yield point (Pa)[a]	0.53	0.60	6.10	0.88	0.76
10 s static gel strength (Pa)	0.51	–	8.18	0.51	0.51
10 min static gel strength (Pa)	10.7	–	20.4	9.2	9.2
After 1 min stirring (Pa)	–	–	–	1.5	3.1

AC: After atmospheric conditioning 30 min at 25 °C.

[a] Estimated by geometrical consideration according to [14].

3.3. Performance tests of conventional oil-well slurries with OnS

3.3.1. Rheological properties

The rheological properties of oil-well cement slurries are important in assuring that the slurries can be mixed at the surface and pumped into the well with minimum pressure drop. In this context, Table 8 shows the rheological properties of different cement slurries studied. In is important to notice that the rheological properties of the slurry CS-9 were too high to be measured after atmospheric conditioning. For this reason the results are not shown in Table 8.

Addition of 0.5% bwoc of OnS cake (0.1% equivalent SiO_2) does not have an adverse effect on the slurry rheology. On the contrary, after atmospheric conditioning, the final rheological properties are slightly decreased compared to the reference Class G slurry based on the lower plastic viscosity (PV) and yield point (YP) determined using the Bingham plastic model. All the YP and PV values derived for the reference (Ref-2) and with 0.5% OnS cake (CS-8) slurries before and after atmospheric conditioning are in the reported range for standard density slurries formulated with Class G according to Shahriar [37].

In the case of the slurries with 5.0% bwoc OnS cake (1.0% equivalent SiO_2) it is evident that the increase in specific surface area in the mix produced an increased yield point of the cement slurry after the initial mixing (0.53 vs. 6.10 Pa). This increase is not excessive and consequently improved the stability or reduced the tendency to settle. This can also be the result of the larger water retention capacity of the OnS agglomerates as already demonstrated in [18]. The higher concentration of nanoparticles results also in an increase in the plastic viscosity which again is expected at constant dispersant content. Furthermore, the gelling capacity of the slurry with 5.0% bwoc of OnS cake (CS-9) was affected to a larger extent based on the gel strength values derived at 10 s and 10 min, Table 8. In general, for a fixed concentration of dispersant, a linear increase in viscosity and yield point is expected. Similar increase in the yield point and plastic viscosity of oil-well cement Class G slurries were already reported by Ershadi et al. [4] using spherical nano-silica powder (20 nm) between 1.0 to 3.0% bwoc.

3.3.2. Free-fluid and slurry sedimentation

The results show that there is no free water in the designed slurries with or without the OnS. The reference slurry in this case was designed to be stable with the addition of an anti-settling biopolymer and clearly the OnS has no detrimental effect, though the water retention and viscosifying effects of OnS are likely masked. As an extension of the

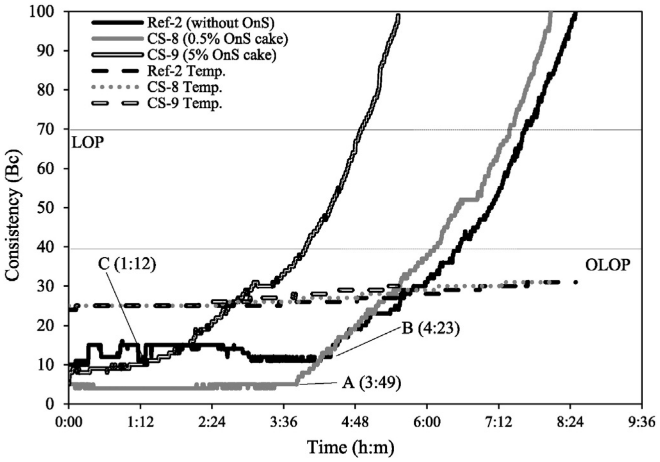

Fig. 2. Thickening time curves of the different conventional cement slurries (1.90 g/cm^3) at 25 °C and 3.5 MPa (temperature and pressure applied in 15 min).

free-fluid test a sedimentation test was also performed to determine the segregation tendency (settling) of the slurries. The density differences obtained, 0.049 and 0.041 g/cm^3 between the top and bottom of Ref-2 and for CS-8, respectively, were within the operational criteria, of a maximum change of 0.060 g/cm^3. This criterion normally changes depending on the cement slurry application [1]. In the case of CS-9 slurry, the sedimentation test was not performed due to the larger YP and PV of this slurry which guarantees higher stability and lower settling.

3.3.3. Thickening-time (TT)

Fig. 2 shows the consistometer curves obtained for the conventional cement slurries. Comparing the slurry without OnS and those containing 0.5 and 5.0% bwoc additions of OnS cake, several observations can be made. First, the slurry with 0.5% bwoc OnS cake, which gives similar PV and YP to the reference, shows consistency values lower than the reference slurry during the first 4 h and 10 min. Although the slurry with 0.5% bwoc of OnS cake gives a relative lower consistency, the point where the slurry starts to build higher consistency values (point A in Fig. 2) is shortened by 33 min compared to the reference (point B, Fig. 2). This is clear evidence of the accelerating effect on the hydration induced by the nano-silica particles. Consistency values obtained at 40 (OLOP) and 70 Bc (LOP) units, define the limits of pumpability, where OLOP is the highest consistency, considered from the operational point of view, that a slurry can be pumped without pressure problems and LOP is the maximum consistency when it is physically impossible to pump a cement slurry according to [38]. As is observed in Fig. 2, low concentrations of OnS marginally decreased the TT at 40 and 70 Bc which amounts to only 15–20 min less than the reference. The higher concentration of OnS cake (5.0% bwoc) has a marked effect on consistency, Fig. 2. Although the consistency is lower in the first 1 h and 38 min, the consistency starts to increase (point C, Fig. 2) almost 2 h 37 min before the reference. This suggests that the OnS can be used as chloride-free accelerator. The acceleration on the cement slurry hydration is also translated into a shorter time to develop consistencies between 40 to 70 Bc. Similar results were reported by Ershadi et al. [4] where additions of 1% bwoc of nano-silica decreased the TT (70 Bc) from 8 h to 1.58 h.

The observed effects of OnS can be used in future for low density slurries that are in general more difficult to stabilize due to the higher water/solid ratio (0.7 to 1.2) normally used. The use of nano-silica in lightweight (0.9 to 1.4 g/cm^3) cement slurries was recently reported by Choolaei et al. [5]. They used a nano-silica with a BET specific surface area of 710 m^2/g (produced by the sol–gel route) as suspending agent for light hollow ceramic microspheres in order to prevent their segregation and to increase the final compressive strength. Additionally, these researchers reported that with the optimum design the effects of nano-silica on the rheological properties can be controlled. Similarly, Salazar [39] used colloidal nano-silica (100 L/kg) with 30% solids as additive to improve the mechanical properties, stability and gas migration control of lightweight slurries (1.63 g/cm^3) on west Venezuelan fields. Finally, the acceleration of TT is an advantage that can be further explored for slurries for low temperature application where consistency development is normally delayed and which is usually compensated by the addition of chloride-based accelerators such as $CaCl_2$, NaCl and KCl. Here, OnS can be used as a chloride free accelerator.

Table 9
Compressive strength of the different conventional (1.90 g/cm^3) cement slurries tested (25 °C-500 psi-15 min).

Compressive strength parameter	TT (h:m)		
	Ref-2	CS-8	CS-9
Time for 0.35 MPa (50 psi)	9:31	9:03	6:20
Time for 3.45 MPa (500 psi)	15:54	15:20	13:20
12-h compressive strength (MPa)	1.19	1.40	2.61
24-h compressive strength (MPa)	9.00	9.47	10.74
48-h compressive strength (MPa)	16.22	16.86	18.91

3.3.4. Ultrasonic-compressive strength (U-CS)

Ultrasonic compressive strength data for conventional slurries is provided in Table 9. Time to reach 0.35 and 3.45 MPa, respectively are considered important from an operational perspective, as a U-CS of 0.35 MPa is related to initial setting [39] while a U-CS of 3.45 MPa is considered as the necessary compressive strength required before operations can continue. From the operational point of view, the compressive strength value at 12, 24 and 48 h is also reported.

According to the U-CS data, Table 9, it is evident that the development of compressive strength is accelerated in the slurries with both 0.5 and 5.0% bwoc OnS cake additions given reduction in times to reach 0.35 and 3.45 MPa. The increase in compressive strength is notable even at the 0.5% bwoc concentration of OnS cake, where the 12-h compressive strength is 16% higher than the reference. This improvement, later decreases with time giving values that are 5.2% and 3.9% higher than the reference slurry at 24-h and 48-h, respectively. In the case of the slurry with 5.0% bwoc OnS cake, the effect is more obvious. The time to reach 0.35 MPa is decreased by 3 h 11 min compared to the reference while the time to obtain 3.45 MPa was 2 h 34 min lower. Furthermore, early compressive strength (12-h) was remarkably improved; it is 119% higher than the reference. Meanwhile at later ages, the 24 and 48-h U-CS values are only 19 and 17% higher than the reference. Similar effect on the ultrasonic compressive strength has been reported by several researchers [4–6].

The previous results demonstrated that the compressive strength of oilwell cement slurries is improved by the addition of 0.1 to 1.0% bwoc of OnS. This means, if the increase in rheological properties can be managed that it is possible to save at least 2 to 3 h of operational time which can be translated in labor cost reduction due to less time waiting for cement to set.

Finally, it is important to clarify that the strength values obtained using API ultrasonic-compressive strength test are indicative of the integrity of the cement under uniaxial loading without confining pressure. This because in ultrasonic-compressive strength measurement, the transit time is correlated using a mathematic derivation and algorithms to estimate compressive strength values in uniaxial mode. In real wellbore conditions and during the well life the cement is subjected to complex triaxial loading, and the failure stresses may be substantially different from those observed in uniaxial standard compressive strength test. To account for these stresses, tensile strength, elasticity and ductility are mechanical parameters currently being determined for the long-term durability of the cement sheath. In general, too high a compressive strength can result in cement with decreased ductility. In this concern, further research is needed to understand the effects of OnS addition on the tensile strength and elasticity of cement sheaths. Other parameters such as friction angle and cohesion should be obtained using different confining pressures (tri-axial test) with the aim to obtain the failure envelope of a cement composition with OnS using the modified Mohr-Coulomb theory [40].

4. Conclusions

In this study, the effects of the different characteristics of OnS as an additive in oil-well cement Class G compositions has been addressed. Cementing mixes were tested using available calorimetric methods and standard procedures. Different modifications in the properties of the cement slurries have been observed which depend on the amount and properties of the OnS used. Based on this observation several conclusions can be drawn and expressed as follows:

1. Although the OnS has different characteristics from colloidal and pyrogenic silica in terms of surface area, silanol groups and morphology, from the macroscopic point of view, the rate and the hydration

degree, activation energy and performance of standard density oil-well cement slurries are similar. This holds for the case in which commercial PCE-type dispersants are applied.

2. Based on the isothermal calorimetric tests and the analysis performed, it is possible to conclude that the OnS acts as an accelerating agent in well cementing slurries. The induction period, the relative setting time and the time to reach the maximum peak of hydration are shortened. Additionally, it was found that, depending on the concentration, the nucleation of aluminate hydrates is also promoted. Finally, it is evident that the pozzolanic activity is also high; based on the fact that the peak heights of the heat flow curves are higher than obtained for pure Class G cement slurries. Comparable results can be found when 0.5% bwoc of OnS is used instead of 10% mS.
3. The isothermal calorimetric tests demonstrated that the temperature, specific surface area (concentration) and type of amorphous silica (OnS vs. mS) for the given w/c ratio (0.44) are the controlling parameters in the hydration behavior of oil-well cement slurries. From the composition of cement slurries, it was found that the Arrhenius law is not suitable to describe the influence of temperature on the rate of cement hydration. Nevertheless, it shows potential to determine the sensitivity to temperature changes in the hydration of cementing slurries with OnS and to validate acceleration effects of additives based on the concept of apparent activation energy (Ea). The activation energy of different cement slurries is first increased (68 kJ/mol) and afterwards decreased by incremental addition of OnS (58 kJ/mol) when these values are compared to the reference (64 kJ/mol). Additionally, it was found that the *Ea* can be calculated according to the hydration degree and time using the incremental method described by [26]. The estimated *Ea* values varied over the temperature range (20–40 and 40–60 °C, respectively) and the early hydration degree ($\alpha = 0.01$) showed values between 38.1 and 43.4 kJ/mol for all tested oil-well slurries.
4. The consistency evolution of oil-well cement slurries with fixed amount of dispersant is affected by incremental additions of OnS which is translated to shorter thickening-time. The addition of 1.0% bwoc of OnS can decrease the thickening-time of conventional Class G cement slurries by almost 2 h 31 min confirming the potential use of OnS as accelerator and viscosifying additive for oil-well applications.
5. The compressive strength of oil-well cement slurries is improved by the addition of 0.1 to 1.0% bwoc of OnS. Both the rate and early compressive strength development are remarkably affected by OnS (16 to 119% more than the reference). The ultimate compressive strength obtained after 48-h of curing was affected to a lower extent (4 to 17% higher). The overall acceleration of the compressive strength development and the shortening in the thickening times (TT) allows drilling operation to resume quickly, lowering waiting on cement times (WOC) and, in consequence, reducing operational cost. Nevertheless, further research is needed to confirm the positive results presented.

Based on the previous feasibility study and conclusion, it is possible to elucidate that higher concentration of OnS could be used with a proper cement slurry design. Finally, it is recommended, for further research, to perform uniaxial and triaxial tests to obtain a better characterization of the mechanical properties of cement slurries containing OnS additions.

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