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# Hydration Kinetics Study of Class G Oil-Well Cement and Olivine Nano-silica Mixtures at 20–60 °C

G. Quercia Bianchi, H.J.H. Brouwers, and K. Luke

**Abstract** In this study the heat evolution of standard density slurries (1.89 g/cm<sup>3</sup>) of Class G oil-well cement and olivine nano-silica additions (0.5–2.0 % bwoc), cured under different temperatures (20–60 °C) and atmospheric pressure, were examined by isothermal calorimetry. Under isothermal and isobaric conditions, the dependency of cement hydration kinetics on curing temperature is related to the activation energy of the cementing slurry. The estimated apparent activation energy of the different slurries with olivine nano-silica varies from 38 to 44 KJ/mol using a dynamic method, at the temperature range of 20–60 °C. It is demonstrated that the addition of olivine nano-silica increases the rate and the heat of hydration of oil-well slurries. These effects are temperature dependent. Finally, comparable hydration degrees were obtained between slurries containing 0.5 % bwoc of olivine nano-silica and 10 % bwoc of oil-well grade micro-silica (mS).

**Keywords** Nano-silica • Olivine • Oil-Well • Cement • Hydration

## 1 Introduction

In oil and gas well construction, one of the most critical processes is that of primary well cementing. Primary well cementing is the process of placing cement in the annular space between the casing and the formation exposed to the drilled wellbore, with the major function to provide zonal isolation. Nano-materials, in particular colloidal silica, are known to improve on the properties of oil well cementing

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compositions [1]. Several methods are used to produce nano-silica, with the two most important commercial processes being neutralization of sodium silicate solutions with acid (colloidal silica) and flame hydrolysis (pyrogenic silica) [2]. These processes are expensive due to the price of the raw materials and the energy requirements involved. As a result of this a more economical method to produce nano-silica has been developed, based on dissolution of olivine (OnS) in acid. Published results [1] on the hydration kinetics and rheological tests of OPC cement pastes with OnS have shown its potential use as an additive to control the viscosity of the slurry, provide thixotropic behavior and possibility to enhance the early compressive strength. However, the effects of adding OnS to a Class G oil-well cement compared to a construction Type 1 cement as well as curing under conditions found typically in well cementing operations have not been studied to date. This paper reports on the use of isothermal calorimetry, as a first approach, to elucidate the effect of OnS on Class G cement slurries.

## 2 Materials and Experimental Methods

An OnS dispersion (synthesized at the pilot scale [1]) with 10.0 wt% solids, equivalent  $\text{SiO}_2$  content of 99.1 wt% and a specific surface area measured by BET method of  $399 \text{ m}^2/\text{g}$  was used. The oil-well cement was a Class G HSR grade as classified by ISO 10426–1 [3]. Oil-well grade micro-silica (mS) with a 94.0 wt% of  $\text{SiO}_2$ , density of  $2.3 \text{ g/cm}^3$  and BET specific surface area of  $19 \text{ m}^2/\text{g}$  was used for comparison with the OnS dispersion. Finally, a commercial dispersant based on modified polycarboxylate ether (PCE-type superplasticizer) with 35 % solids content and a density of  $1.095 \text{ g/cm}^3$  was used for the calorimetric study. Distilled water was used in all experiments. A total of eight oil-well cement slurries with a normal density of  $1.89 \text{ g/cm}^3$  ( $15.79 \text{ lbm/gal}$ ) were prepared according to the designs shown in Table 1. Slurry preparation consisted of adding dispersant and OnS or powder micro-silica to water in a high energy (600 W) hand blender (Philips HR 1363) at 20 s intervals. This was followed by addition of the cement over a 15 s period and then continuing mixing for an additional 1 min to obtain a homogeneous slurry. The formulated slurries were studied using an isothermal calorimeter (TAM® Air TA Instruments) at 20, 40 and 60 °C over a period of 48 h.

**Table 1** Slurry designs used for hydration kinetic studies (density  $1.89 \text{ g/cm}^3$ )

Materials	Ref-1	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
OnS-15 (% bwoc) <sup>a</sup>	0	0.5	1.0	1.5	2.0	0	0	0
Micro-silica (% bwoc)	0	0	0	0	0	1.0	2.0	10.0
Class G HSR (%)	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
Dispersant (gal/sk) × 100	6	6	6	6	6	6	6	6
w/b	0.44	0.44	0.44	0.44	0.45	0.44	0.44	0.41

<sup>a</sup>Equivalent  $\text{SiO}_2$  content. Sk: 1 cement sack = 94 lbm (42.64 kg)

The progress of the hydration of the cement slurries was quantified by the hydration degree ( $\alpha$ ), which varies from 0 to 1. For this study, the hydration degree is estimated according to [4] 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 [5] using the cement composition and amount and type of silica. The maximum heat of olivine nano-silica or micro-silica was assumed to be equal from the amount of amorphous  $\text{SiO}_2$  in both silica types (amount to 780 J/g according to [6]). The activation energy ( $E_a$ ) was estimated using two different methods. The first method applied was considering a first order reaction rate (Arrhenius-type) expression as follows:

$$k = A \cdot e^{\frac{-E_a}{RT}} \quad (1)$$

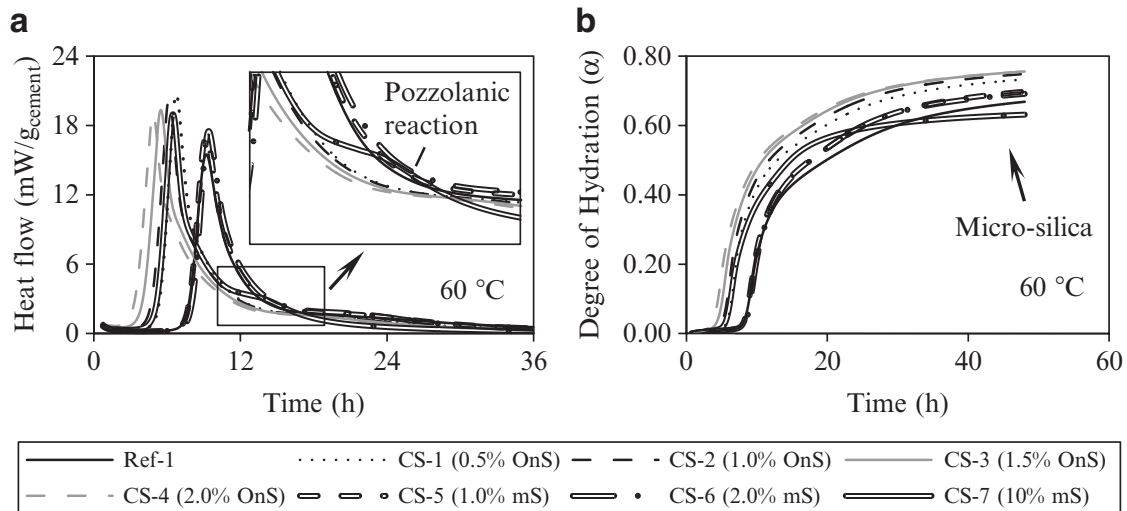
where  $R$  equals the natural gas constant (8.314 J/mol/K),  $T$  equals the temperature in K at which reaction occurs,  $k$  equals the rate of heat flow evolution ( $dH/dt$ ),  $A$  equals the proportionality constant (same units as  $k$ ), and  $E_a$  equals the activation energy (J/mol). In the 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  $E_a$ , the methodology described by [7] 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) [5]. In this method the reaction rate 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 [8] as follows:

$$E_a(\alpha) = R \left[ \frac{T_1 T_2}{T_1 - T_2} \ln \left( \frac{\frac{d\alpha_1}{dt}}{\frac{d\alpha_2}{dt}} \right) \right] \quad (2)$$

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 20–60 °C was considered.

### 3 Results and Discussion

From the heat flow curves (Fig. 1a) the hydration degree ( $\alpha$ ) of the different cement slurries studied was calculated (Fig. 1b). It is interesting that the final estimated  $\alpha$  of 10 % mS slurry is the lowest in the tested range of temperatures (20–60 °C). The lowest hydration degree for 10 % mS 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 confirms again the acceleration effect



**Fig. 1** Examples of obtained results at 60 °C of the different cement slurries (normal density 1.89 g/cm<sup>3</sup>), (a) heat flow curves and (b) estimated hydration degree curve

**Table 2** Estimated hydration degree ( $\alpha$ ) for the different cement slurries (normal density 1.89 g/cm<sup>3</sup>) tested at 20 °C, 40 °C and 60 °C, respectively

Slurry	$\alpha$ (12 h)	20 °C			40 °C			60 °C		
		$\alpha$ (24 h)	$\alpha$ (48 h)	$\alpha$ (12 h)	$\alpha$ (24 h)	$\alpha$ (48 h)	$\alpha$ (12 h)	$\alpha$ (24 h)	$\alpha$ (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	

induced by the OnS additions. In general, the higher the temperature the higher the hydration degree for OnS slurries. Table 2 summarizes the calculated hydration degrees at 12, 24 and 48 h, for all the cement slurries tested. It is possible to observe from the data in this table that a small addition of OnS (0.5 % bwoc) has the same effect as 10 % bwoc of micro-silica. Higher  $\alpha$  after 12 h results in cost reductions due to the decrease in waiting time to continue the drilling operations due to cementing operations. Also, 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 ( $E_a$ ) 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

**Table 3** Estimated average activation energy ( $E_a$ ) of the different cement slurries (normal density 1.89 g/cm<sup>3</sup>)

Slurry	Slope method (static)	Incremental method (dynamic)	Incremental method (dynamic)
	$E_{a_{20-40-60}}$ (kJ/mol)	$E_{a_{20-40}}$ (kJ/mol)	$E_{a_{40-60}}$ (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)

in Table 3. It is evident from the data presented in Table 3 that the  $E_a$  obtained by the slope method is different for all slurries. In the case of the OnS slurries, the  $E_a$  increases for 0.5 and 1.0 % bwoc OnS slurries (CS-1 and CS-2) compared to the reference, after that the  $E_a$  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 obtained results. First, the drop in the activation energy, in general, confirms the acceleration effect induced by nano-silica particles.

Lower  $E_a$  means that the hydration reaction is enhanced or can occur easier. Also, according to [9], reactions with high  $E_a$  are very temperature-sensitive. On the contrary, reactions with low  $E_a$  are relatively temperature-sensitive. Based on this, it is possible to state that the addition of OnS and mS in concentrations lower than 2.0 % bwoc make the hydration reaction of Class G HSR 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 of this can be found in changes induced by the presence of nano-particles in the stoichiometry, kinetics and mechanism of cement hydration reaction [9]. Cement is composed of a number of different phases that react at different rates, so it is possible that the  $E_a$  may vary considerably as with the hydration degree [5]. Furthermore, hydration is initially reaction-rate-limited and becomes diffusion-limited as solid hydration products are formed [10]. For that reason an incremental calculation method was also applied to highlight how  $E_a$  is influenced by the progress of hydration (Table 3). The average  $E_a$  for slurries with OnS is slightly affected compared to the reference slurry. Nevertheless, considering the instantaneous  $E_a$  calculated at very early age ( $\alpha=0.01$ ) which is represented by the values in parenthesis in Table 3, it is possible to observe that the  $E_a$  is lower than the reference. This confirms again the role of OnS to decrease the  $E_a$  and thus, accelerating the slurry's setting. The same observation is valid for mS slurries which also decrease  $E_a$ . In Table 3 it is also possible to observe that the apparent activation energy varies with the temperature ( $E_{a_{20-40}} < E_{a_{40-60}}$ ). According to [8] 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 [6]. Further studies [5, 11] attributed the change of  $E_a$  with temperature rise. The fast initial hydration caused by high temperature leads to the formation of a thicker and more compact layer of hydration products (changes in microstructure level) around the cement grains that affects the hydration (increasing  $E_a$ ).

## 4 Conclusions

In this study, the influence of olivine nano-silica (OnS) in the hydration behavior of oil-well Class G HSR cement has been addressed. Cementing mixes were tested using available calorimetric methods. Modifications in the cement degree of hydration and activation energy have been observed. The test results demonstrated that the temperature, specific surface area (concentration) and type of amorphous silica (OnS vs. mS) for the given w/b ratio are the controlling parameters. Based on these observations it is concluded that the OnS acts as an accelerating agent in well cementing slurries. Finally, comparable hydration degrees were obtained between slurries containing 0.5 % bwoc of OnS and 10 % bwoc of oil-well grade mS.

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