Effect of Nanosilica on Cement Hydration under High Temperature and Pressure

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ABSTRACT

Hydration of cement slurries in oil well cementing takes place under high temperature and pressure. The use of nanosilica to alter cement hydration in oil wells is investigated. Cement pastes with water to binder ratio (w/b) of 0.45 and 1-3% by weight nanosilica were prepared. The cement pastes were hydrated under two curing conditions, room condition (20°C with 0.1 MPa pressure) and an elevated temperature and pressure conditions (80°C with 10 MPa pressure) for 7 days. Calcium-silicate-hydrates (C-S-H) polymerization of the hydrated cement pastes was investigated using X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) methods respectively. The results showed that 1% nanosilica by weight of cement produced the highest level of C-S-H polymerization under room conditions while 3% nanosilica under elevated curing conditions achieved the highest level of C-S-H polymerization. A threshold of nanosilica contents based on curing conditions is proposed considering the significance of cement polymerization on strength and ductility of hydrated cement pastes.

Keywords: NMR, XRD, Nanosilica, CSH polymerization

1. Introduction

Recent studies have shown that there is a great potential to improve the mechanical characteristics of cement paste by incorporating nanosilica, nanoalumina and carbon nanotubes [1-3]. Developments in nanotechnology over the past few years have paved the way for developing new materials that can alter the properties of cement-based mortar and concrete. Early efforts in nanotechnology were directed to understand the phenomenon of cement hydration and cement degradation mechanisms [4]. Studies in nano-modified cements, self-healing cement and other nano-based cementitious materials have been in progress over the last decade [5]. It has been shown by several researchers that traditional cement based materials showed radically enhanced properties when engineered at the nanoscale [6]. Moreover, nanoparticles such as TiO_2, ZnO_2, fullerenes, carbon nanotubes, silica, alumina, magnesium, calcium and clays have been examined to alter workability, strength, stiffness and energy absorption characteristics of cementitious composites [3, 6].

In this study, an investigation was conducted with the objective of understanding the significance of elevated temperature and pressure curing conditions on the hydration of Type II ordinary Portland cements (OPC) in the presence of nanosilica. OPC pastes with water to binder ratio (*w/b*) 0.45 with and withour nanosilica contents of 1% and 3% are hydrated for 7 days under two conditions: room condition of 20 °C and 0.1 MPa pressure and an elevated condition of 80 °C with 10 MPa pressure. Using ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR), the silicate polymerization of hydrated cement is investigated. The microstructural compounds in the hardened cement pastes are also investigated by X-ray diffraction (XRD) analysis. The mechanical characteristics of the microstructural phases in the

hardened cement pastes represented by the modulus of elasticity are investigated using nanoindentation. The results shed light on the effect of curing conditions on cement hydration.

2. Experimental Study

2.1. Materials

Type II OPC, known as low temperature and sulfate resistance cement [7, 8] was used for all cement paste specimens. The nanosilica used is AEROSIL® 380, which has average BET surface area of 380 m^2/g and average particle diameter of 7 nm. A water/binder (*w/b*) ratio of 0.45 was used for all specimens. Two cylinders, ϕ 10 mm × 10 mm height, for each nanosilica contents of 0%, 1% and 3% were prepared for two curing conditions. The procedures for mixing the hydraulic cement pastes followed the ASTM standards [9]. The specimens were molded in a tube for one day and then cured in the corresponding curing condition for 6 days. The rationale behind selecting the curing period conditions was to simulate field conditions of oil well cement (OWC) based on published literature [10-12].

2.2. Curing conditions

For room curing conditions, specimens were cured under tap water with a controlled temperature of 20 °C and pressures 0.1 MPa (1 atm). For elevated temperature and pressure curing conditions similar to deep oil well condition, a special set-up for the elevated temperature of 80 °C and pressure of 10 MPa (98.7 atm) was prepared. 450 ml *Parr®* pressure vessel was used. 300 ml of tap water filled the vessel and specimens were cured in the water under elevated temperature and pressure. Using the heater surrounding the vessel, temperature was elevated and kept constant during the curing time period. To prevent temperature fluctuations in the vessel, 20 °C cooling water was circulated through the cooling loop in the vessel. Pressure was applied by injecting nitrogen gas from a compressed Nitrogen cylinder at 10 MPa.

2.3.Testing Procedures

2.3.1. X-ray diffraction (XRD)
XRD is a well-known methodology in studying cement chemistry [13] and is used to detect various crystalline phases in hydrated cement. Using XRD spectra, several compounds in hydrated cement paste such as alite (C_3S), belite (C_2S), ettringite (AF_t), calcium hydroxide (CH, portlandite) and calcium silicate hydrate: tobermorite (C-S-H,) can be detected. There exists a wealth of information in the literature on XRD observations of cement hydration products [13-15].

2.3.2. Nuclear magnetic resonance (NMR)
A silicate tetrahedron having the number of *n* sharing oxygen atoms is expressed as Q^n where *n* is the number sharing oxygen atoms ranging from zero to four. The intensity of the silicate Q connections, used to estimate degree of silicate polymerization, can be investigated using ^{29}Si MAS NMR technique. Q^0 is observed due to the remaining alite: tricalcium silicate (C_3S) and belite: dicalcium silicate (C_2S) in hydrated cement while Q^1 (end-chain group), Q^2 and Q^3 (middle-chain group) in silicate are typically detected due to the layered structure of calcium silicate hydrates (C-S-H), which makes up 67% of cement hydration product. Q^4 is the polymerized quartz and can be observed in silica rich products such as fly ash, silica fume and nanosilica. Using the intensity fractions of Q^ns, the degree of hydration D_h of a hydrated cement paste can be calculated after Bell et al. [16]

$$D_h = Q^1 + Q^2 + Q^3 \tag{1}$$

If a silica rich material is used in cement paste, the pozzolanic activity coefficient D_{pa} is calculated by comparing the intensity fraction of Q^4 at time t_0 and t after Jupe et al. [10]

$$D_{pa} = \frac{Q^4(t_0) - Q^4(t)}{Q^4(t_0)} \qquad (2)$$

Assuming that nanosilica is pure silicon dioxide (SiO_2), the initial intensity fractions of Q^4 at time t_0 for Type II OPC pastes with w/b of 0.45 incorporating 1% and 3% nanosilica are estimated as 4.4% and 12.2% respectively. The average degree of C-S-H connectivity D_c, which can represent the silicate polymerization, in a hydrated cement paste is also calculated after Jupe et al. [10]

$$D_c = \frac{Q^1 + 2Q^2 + 3Q^3}{Q^1 + Q^2 + Q^3} \qquad (3)$$

High values of D_c represent high polymerization of C-S-H.

^{29}Si MAS NMR spectroscopy was performed in 7 mm cylinders spun at 4 kHz. Approximately 10,000 scans were performed on each sample. The ^{29}Si chemical shifts are respectively referenced relative to tetramethylsilane $Si(CH_3)_4$ (TMS) at 0 ppm, using $Si[(CH_3)_3]_8Si_8O_{20}$ (Q8M8) as a secondary reference (the major peak being at 11.6 ppm relative to TMS).

2.3.3. Nanoindentation

Nanoindentation was performed using a vertical nanoindenter NanoTest™ system equipped with a Berkovich tip. The applied load is 0.55 mN including 0.05 mN preloading. Specimens were casted in acrylic to fit them into the nanoindentation holder. The specimens were then polished on a Buehler Ecomet 3 polisher with a Buehler Automet 2 power head. The polishing was performed using 125-micron diamond pad first and then at the order of 70-, 30-, 9- and 1-micron diamond pad for 10, 15, 15, 30 and 60 minutes respectively. Fifty indentations on each specimen were performed in five rows spaced at 1000 μm between the rows and 200 μm spacing between individual indentations. The results were analyzed to identify the elastic modulus of the different microstructural phases.

3. Results and Discussions

The difference in microstructure as a result of the different curing conditions is examined first using XRD analysis. As shown in Fig. 1, sharp portlandite (CH) peaks at 18.2° (2θ) are apparent in the XRD spectra of hydrated cement pastes cured under elevated curing conditions. The quartz (nanosilica) peak at 36.5° (2θ) disappears in the XRD spectrum of hydrated cement pastes incorporating 1% nanosilica in elevated curing condition as shown in spectra (c) and (d) in Fig.1. This is more apparent for hydrated cement pastes incorporating 3% nanosilica. The three quartz (nanosilica) peaks at 25.7°, 36.5° and 45.8° (2θ) are absence from the XRD spectrum for hydrated cement pastes incorporating 3% nanosilica in elevated curing conditions as shown in spectra (a) and (b) in Fig.1. More alite (C_3S) and belite (C_2S) known to contribute for late strength of cement paste are consumed under elevated curing conditions as alite peaks appear at 29.2° and 32.9° (2θ) and belite peaks appear at 18.9° and 31° (2θ) in room curing conditions and decreases in specimens cured under elevated curing conditions as shown in spectra (c) and (d) in Fig.1 for 1% nanosilica paste. There is also evidence of more consumption of alite (C_3S) and belite (C_2S) in elevated curing conditions for 3% nanosilica paste with the complete disappearance of peaks at 29.2° and 31° (2θ) respectively as shown in spectra (a) and (b) in Fig.1. These observations confirm that the threshold of nanosilica

contents for effective pozzolanic reaction seems to increase when the cement paste is cured under elevated temperature and pressure rather than under room conditions. Moreover, the hydration of cement paste is obviously accelerated under elevated curing conditions based on the consumption of alite and belite and the relatively high intensity of CH peaks in XRD spectra of hydrated cement paste specimens cured under room conditions.
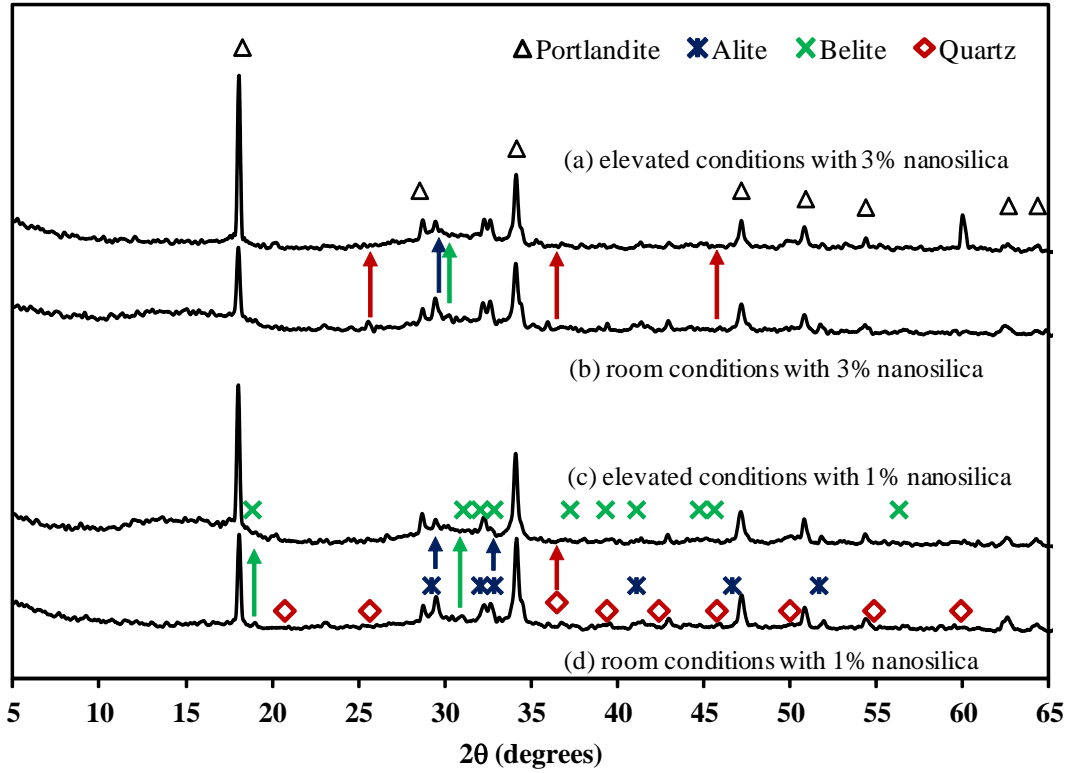

Fig. 1. XRD spectra of 1% and 3% nanosilica pastes cured under room and elevated conditions.

The resulting ^{29}Si MAS NMR spectra were deconvoluted and presented in Fig.2. The effects of nanosilica and different curing conditions on the degree of hydration in Eq. (1), the pozzolanic activity in Eq. (2) and the degree of C-S-H connectivity in Eq. (3) were examined. The integration results of the Q^n intensities by deconvolution are presented in Table 1. Q^3 level of polymerization was found in cement pastes with 1% and 3% nanosilica cured under high temperature and pressure. However, Q^4 level of polymerization was only observable in cement paste with 3% nanosilica under room curing conditions due to the unreacted nanosilica.

Table 1. Integration of Q^n intensities by deconvolution of ^{29}Si MAS NMR

Specimens	Q^n (%)					D_h (%)	D_{pa} (%)	D_c
	Q^0	Q^1	Q^2	Q^3	Q^4			
No nanosilica-rm	44	36	20	-	-	56.0	-	1.36
1% nanosilica-rm	29	39	30	-	2	69.0	54.8	1.43
3% nanosilica-rm	35	33	24	-	8	57.0	34.4	1.42
No nanosilica-elv	22.3	37.4	40.3	-	-	77.7	-	1.52
1% nanosilica-elv	22	37	36.9	4	0.1	77.9	97.7	1.58
3% nanosilica-elv	22	35	37.9	5	0.1	77.9	99.2	1.61

D_h is degree of hydration: Eq. (1).
D_{pa} is degree of pozzolanic activity: Eq. (2).
D_c mean silicate chain length: Eq. (3).
'-rm' means room curing conditions. '-elv' means high temperature and pressure curing conditions

For the effects of nanosilica contents on the degree of hydration of cement, the highest degree of hydration under room curing conditions was 69% and occurred with cement paste specimens incorporating 1% nanosilica. However, the degrees of hydration under elevated curing conditions were 78% for all three cases. For the average degree of connectivity (polymerization), the highest degree of polymerization of 1.61 occurred with cement paste specimens incorporating 3% nanosilica cured under elevated curing conditions. The highest degree of connectivity under room curing conditions of 1.43 occurred with cement paste specimens incorporating 1% nanosilica. The pozzolanic activity is calculated using Eq. (2). It is that the pozzolanic activity significantly increased under elevated curing conditions compared with room curing conditions. While the pozzolanic activities changed from 54.8% to 34.4% due to increasing the nanosilica content from 1% to 3% under room curing conditions, there was no significant difference in the pozzolanic activities due to increasing the nanosilica content from 1% to 3% under elevated curing conditions. This can be explained by realizing that under elevated curing conditions most nanosilica is reacted independent of its content.
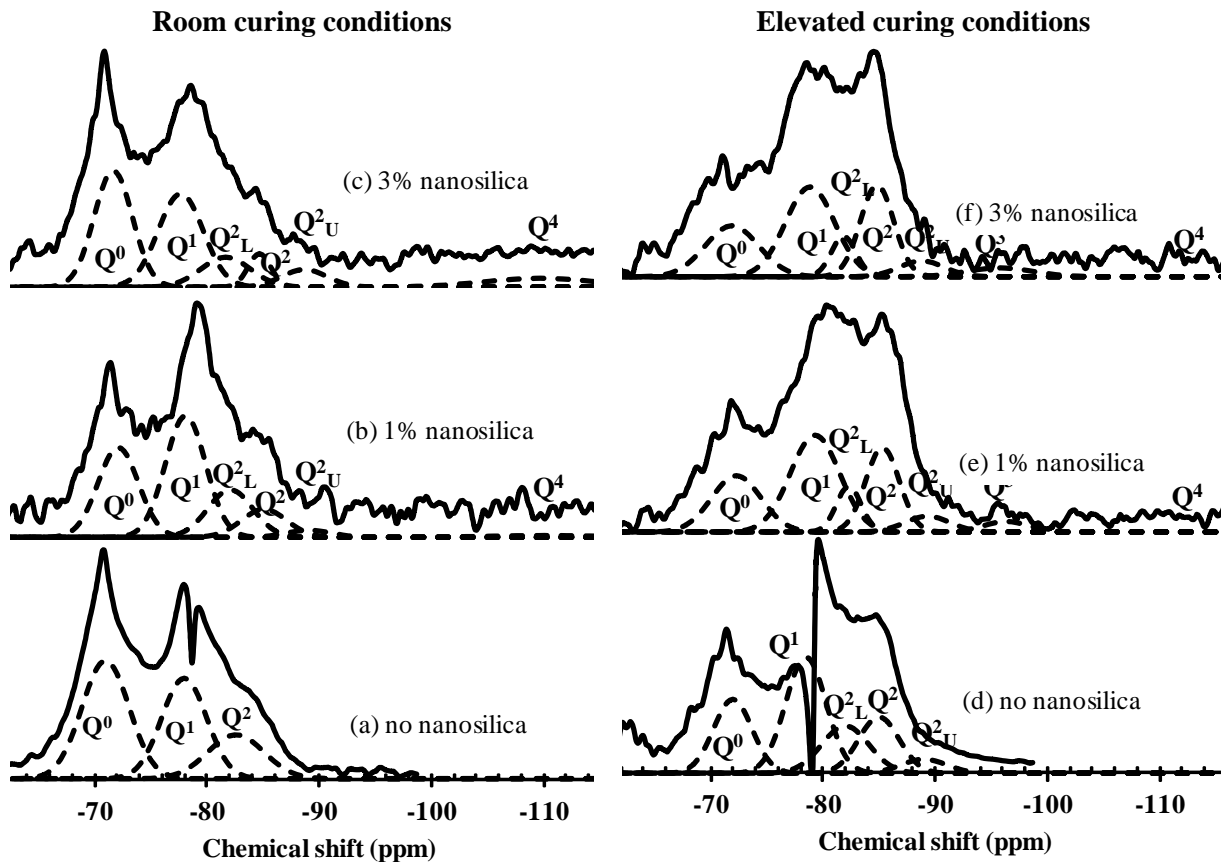

Fig. 2. NMR spectra of 0, 1% and 3% nanosilica cured under room and elevated conditions.

The distribution of the modulus of elasticity is deconvoluted and the results are summarized in Table 2. The degree of hydration was calculated based on the identified volume fraction of unhydrated cement particles. While microstructural phases identified from our nanoindentation experiments were reported by other researchers [17-19], the analysis indicated one unknown relatively stiff phase that was not reported in the literature before. For the cement pastes cured in elevated conditions for 7 days, LD-C-S-H occupies close to half of the hydration products of the cement paste without nanosilica (39% for No nanosilica-elv in Table 2) while the LD-C-S-H fraction in hydration products of the cement paste incorporating nanosilica decreases significantly and a stiff 'new phase' appears (8% for 1% nanosilica-elv and

14% for 3% nanosilica-elv in Table 2). This unknown phase appeared only in the cement paste incorporating nanosilica cured under elevated curing conditions as shown in Table 2. When this relatively stiff *'new phase'* in Table 2 is considered, the degree of hydration calculated from nanoindentation results agrees well with that extracted from ^{29}Si MAS NMR. This observation suggests that there might be other sub-microstructural phases than those reported in the literature to be realized but might be highly dependent on curing conditions and silica source. Further research is warranted to confirm the existence of such relatively stiff *'new phase'* in hydrated cement pastes with nanosilica cured under elevated curing conditions.

Table 2. Microstructural phase fractions from deconvolution of nanoindentation results

Phases	Ettr.	LD-CSH	HD-CSH	CH	New Phase	U1	U2	D'_h
E range (GPa)	4~6	18~21	28~31	39~43	52~59	53~62	82~119	
No nanosilica-rm	2%	23%	15%	18%	-	34%	8%	58%
1% nanosilica-rm	4%	20%	25%	20%	-	23%	8%	69%
3% nanosilica-rm	2%	16%	20%	21%	-	33%	8%	59%
No nanosilica-elv	2%	39%	18%	21%	-	14%	6%	80%
1% nanosilica-elv	4%	8%	12%	24%	26%	-	26%	74%
3% nanosilica-elv	4%	14%	20%	28%	8%	-	26%	74%

U1and U2 represent unhydrated cement particles.

D'_h is the degree of hydration calcuated by extracting fractions of U1 and U2 from 100%.

4. Conclusion

XRDA, ^{29}Si MAS NMR and nanoindentation experiments were done for the cement pastes without and with 1% and 3% nanosilica hydrated under two curing conditions, 20 °C with 0.1 MPa pressure and 80 °C with 10 MPa pressure, for 7 days to examine the microstructural compositions and the silicate polymerization. The results showed that the hydration of cement paste is faster and the average degree of polymerization is higher under elevated curing conditions than under room curing conditions. The results also showed the relatively higher pozzolanic activity of nanosilica under elevated curing conditions than under room curing conditions. This indicates that the threshold of nanosilica contents for effective pozzolanic reaction seems to increase when the cement paste is cured under elevated temperatures and pressures rather than those done under room conditions and as such, relatively high nanosilica content (over 3%) can be used for OWC of oil well operations in elevated temperature and pressure conditions to enhance the quality of the cement lining. The observation of a relatively stiff hydration product from nanoindentation experiments of hydrated cement pastes incorporating nanosilica cured under elevated conditions, denoted as 'new phase' in this study, suggests that there might be other sub-microstructural phases of C-S-H than those reported earlier in the literature. Further research is necessary to confirm these observations and to understand the role these sub-microstructural phases of C-S-H play in forming cement strength and durability.

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