Curing and Piezoresistive Behaviors of Smart Cement Modified with Silica Nanoparticles Using Vipulanandan Models for Multiple Applications

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Abstract:There is increasing interest in evaluating the impacts of adding nanoparticles on the behavior of highly sensing smart cement. There is also interest in how to integrate the smart cement in new constructions and in-service infrastructures. In this study, highly sensing chemo-thermo- piezoresistive smart cement was modified with up to 1% silicon dioxide nanoparticles (Nano Silica - $\mathrm{NanoSiO_2}$) to evaluate the effects not only on the sensing properties but also the curing and compressive piezoresistive stress-strain relationship and strength. Smart cement was prepared by adding 0.1% carbon fibers (CF) based on the cement weight and new Vipulanandan piezoresistive theory to make the cement a piezoresistive but still a nonconductive material. Testing evaluated the smart cement behavior with and without $\mathrm{NanoSiO_2}$ in order to verify the sensitivity of electrical resistivity changes with curing time and compressive loading. The addition of 0.5% and 1% $\mathrm{NanoSiO_2}$ increased the initial electrical resistivity of the smart cement by 17% and 35% respectively, hence electrical resistivity a material property that can be used as a quality control parameter for mixing in the field. The addition of 1% $\mathrm{NanoSiO_2}$ increased the compressive strength of the smart cement by 14% and 42% after 1 day and 28 days of curing respectively. The Vipulanandan p-q curing model predicted the changes in electrical resistivity with curing time very well. The Vipulanandan p-q stress- piezoresistive strain model predicted the experimental results very well. For the smart cement modified with $\mathrm{NanoSiO_2}$, the resistivity change at peak stress was over 1250 times (125,000%) higher than the change in the compressive strain. Also, a linear correlation was obtained between the $\mathrm{RI_{24hr}}$ and the compressive strength of the $\mathrm{NanoSiO_2}$ modified smart cement based on the curing times.

Keywords: Smart cement, Electrical resistivity, Piezoresistivity, Vipulanandan models.

Introduction

In the construction industry and petroleum industry, cement has been used for multiple applications and there is need for further enhancement of the sensing properties and mechanical properties of the cement. In the construction industry it is used as a binder in various types of grouts and concrete to construct deep foundations, pipes, bridges, highways, storage facilities and buildings. In the oil industry cement is typically utilized to fill the annular space between the casing and rock formation by displacing the drilling fluid. Also, cement will support the casing and protect it against corrosion and impact loading, restrict the movement of fluids between formations, and isolate productive and nonproductive zones. The strength of cement usually depends on factors such as time and conditions of curing, environmental conditions, slurry design and use of additives and any additional treatments to the cement. One of the important additives that has been used in cement is silica, which has been used in a certain amount to mitigate the strength degradation [1-2]. Also, monitoring cement curing under various environments is critical to ensure hydration of the cement and also prevent failures during constructions [3-10].

Objectives

The overall objective was to investigate the effect of up to 1% of NanoSiO$_2$ on the modified smart cement behavior. The specific objectives were as follows:

1 Investigate and quantify the changes in the electrical resistivity during the curing time and compressive behavior of the NanoSiO$_2$ modified smart cement.

2 Model the curing and compressive piezoresistive behavior of the NanoSiO$_2$ modified smart cement

Materials and Methods

In this study, cement with water-to-cement of 0.4 was used. To improve the sensing properties and piezoresistive behavior of the cement modified with less than 0.1% of carbon fibers (CF) and up to 1% nanosilica by the weight of cement was mixed very well for all the samples (no change in cement resistivity). After mixing, specimens were prepared using cylindrical molds with diameter of 50 mm and a height of 100 mm. Two conductive wires were placed in all of the molds to measure the changing in electrical resistivity. At least three specimens were prepared for each mix.

Silicon dioxide nanoparticle (NanoSiO$_2$)

Silicon dioxide nano powder(NanoSiO$_2$) with the grain size of 12 nm, specific surface area of 175 to 225 m^2/g (from supplier datasheet) was selected for this study.

Electrical Resistivity

It was very critical to identify the sensing properties for the cement that can be used to monitor the performance. After numerous studies and based on the current study on cements, electrical resistivity (ρ) was selected as the sensing property for cement-based materials. Hence two parameters (resistivity and change in resistivity) were used to quantify the sensing properties of cement. Electrical resistivity is given by:

$$\rho = R/K_e \tag{1}$$

where R is electrical resistance, and Ke is the effective correlation parameter. In the literature the nominal correlation parameter (developed for conductors) Kn which is equal to the ratio L/A where L is the linear distance between the electrical resistance measuring points, A is the effective cross sectional area. Current study has shown that the Ke was in the range of 50 to 55 while the Kn was in the rage of 25 to 30. Normalized change in resistivity with the changing conditions is represented as

$$\frac{\Delta\rho}{\rho_o} = \frac{\Delta R}{R_o} \tag{2}$$

where Ro, ρ_o: Initial resistance and resistivity respectively and ΔR, $\Delta\rho$: change in resistance and change in resistivity respectively.

Initial Resistivity of Smart Cement Slurry

Two Different methods were used for electrical resistivity measurements of the cement slurries. To assure the repeatability of the measurements, the initial resistivity was measured at least three times for each cement slurry and the average resistivity was reported. The electrical resistivities of the cement slurries were measured using conductive probe and digital resistivity meter used in the oil industry.

Resistivity of smart cement

In this study high frequency AC measurement was adopted to overcome the interfacial problems and minimize the contact resistances. Electrical resistance (R) was measured using LCR meter (measures the inductance (L), capacitance (C) and resistance (R)) during the curing time. This device has a least count of $1\mu\Omega$ for electrical resistance and measures the impendence (resistance, capacitance and inductance) in the frequency range of 20 Hz to 300 kHz. Based on the impedance(z) - frequency(f) response it was determined that the smart cement was a resistive material [4,6,7,8,9]. Hence the resistance measured at 300 kHz using the two-probe method was correlated to the resistivity (measured using the digital resistivity device) to determine the Ke factor (Eqn.1) for a time period of initial five hours of curing. This Ke factor was used to determine the resistivity of the cement with the curing time.

Piezoresistivity Test

Piezoresistivity describes the change in electrical resistivity of a material under stress. Since oil well cement serves as pressure-bearing part of the oil and gas wells in real applications, the piezoresistivity of smart cement (stress-resistivity relationship) with different w/c ratios were investigated under compressive loading at different curing times. During the compression test, electrical resistance was measured in the direction of the applied stress. To eliminate the polarization effect, AC resistance measurements were made using a LCR meter at frequency of 300 kHz [8].

Statistical Parameters

In order to determine the accuracy of the model predictions, both coefficient of determination (R^2) and the root mean square error (RMSE) were used.

RESULTS AND DISCUSSION

Resistivity

Several characteristic resistivity parameters can be used in monitoring the curing (hardening process) of the cement. The parameters are initial resistivity (ρ_o), minimum electrical resistivity (ρ_{min}),time to reach the minimum resistivity (t_{min}) and percentage of maximum change in resistivity at the end of 24 hours (RI_{24hr}) is defined in Eqn.(3) as follows:

$$RI_{24hr} = (\frac{\rho_{24hr} - \rho_{min}}{\rho_{min}})100 \qquad (3)$$

Curing

Change in the electrical resistivity with time and the minimum resistivity quantifies the formation of solid hydration products, which leads to a decrease in the porosity which influences the cement strength development.

Vipulanandan curing model

Based on experimental results, model proposed by Vipulanandan was used to predict the electrical resistivity of smart cement during hydration up to 28 days of curing as shown in Figure 5. The curing model is defined as follows:

$$\frac{1}{\rho} = \left(\frac{1}{\rho_{\min}}\right) \frac{\left(\frac{t+t_o}{t_{\min}+t_o}\right)}{q_1+(1-p_1-q_1)\left(\frac{t+t_o}{t_{\min}+t_o}\right)+p_1\left(\frac{t+t_o}{t_{\min}+t_o}\right)^{\frac{q_1+p_1}{p_1}}} \qquad (4)$$

where ρ: electrical resistivity ($\Omega-$m); ρ_{min}: minimum electrical resistivity($\Omega-$m); t_{min}: time corresponding minimum electrical resistivity (ρ_{min}); p_1, t_o, and q1 are model parameters; and t:time (minutes).

Smart Cement

The minimum resistivity (ρ_{min}) of smart cement was 0.85 Ωm and the time to reach the minimum resistivity (t_{min}) was 99 minutes as summarized in Table 1. The resistivity after 24 hours was 3.90 Ωm, representing a change of about 268% in 24 hours. The resistivity index (RI_{24hr}) for smart cement were 364%, represents the maximum resistivity change in 24 hours as summarized in Table 1. The resistivity after 7 days and 28 days were 7.7 Ωm and 35.7 Ωm respectively and also shown in Figure 1. These observed trends clearly indicate the sensitivity of resistivity to the changes occurring in the curing of cement as summarized in Table 1.

Table 3: **Curing Bulk Resistivity Parameters for the Smart Cement with NanoSi$_2$**

NanoSi$_2$ (%)	**Initial resistivity, ρ_o (Ω·m)**	$\rho_{\min}$ **(Ω·m)**	$t_{\min}$ **(min)**	ρ_{24hr} **(Ω·m)**	ρ_{7days} **(Ω·m)**	**RI$_{24hr}$ (%)**	**RI$_{7days}$ (%)**
0	1.06 ± 0.02	0.85 ± 0.02	99 ± 5	3.90 ± 0.04	7.7 ± 0.5	364	806
0.5	1.20 ± 0.03	0.95 ± 0.05	110 ± 7	4.16 ± 0.01	8.0 ± 0.4	338	708
1	1.39 ± 0.03	1.11 ± 0.03	122 ± 4	4.76 ± 0.03	8.7 ± 0.8	328	684

Smart Cement with 0.5% NanoSiO$_2$

The minimum resistivity (ρ_{min}) of smart cement with 0.5% NanoSiO$_2$ was $0.95\Omega - m$, which was 12% higher compared to the smart cement minimum electrical resistivity. The time to reach the minimum resistivity (t_{min}) was 110 minutes as summarized in Table 1 and it was 11% higher than the smart cement. The resistivity after 24 hours was 4.16 Ωm, representing a change of about 289 % in 24 hours as shown in Figure 1. The resistivity index (RI_{24hr}) for smart cement with 0.5% NanoSiO$_2$ was 338% as summarized in Table 1. The resistivity after 7 days and 28 days were 8.0 Ωm and 27.8 Ωm respectively and also shown in Figure 1. Change in RI_{24hr} decreased with the

0.5% NanoSiO$_2$ content. These observed trends clearly indicate the sensitivity of resistivity to the changes occurring in the curing of cement as summarized in Table 1.

Smart Cement with 1% NanoSiO$_2$

The minimum resistivity (ρ_{min}) of smart cement with 1% of NanoSiO$_2$ 1.11 $\Omega - m$, which was about 30% higher compared to the smart cement minimum electrical resistivity. The time to reach the minimum resistivity (t_{min}) was 122 minutes as summarized in Table 1 which was about 23% higher than the smart cement. The resistivity after 24 hours was 4.76 Ωm , representing a change of about 242 % in 24 hours as shown in Figure 1. The resistivity after 7 days and 28 days were 8.7 Ωm and 20.6 Ωm respectively and also shown in Figure 1. The resistivity index (RI_{24hr}) for smart cement with 1% of NanoSiO$_2$ was 328% as summarized in Table 1.

Change in RI_{24hr} decreased with 1% NanoSiO$_2$ content. These observed trends clearly indicate the sensitivity of resistivity to the changes occurring in the curing of cement as summarized in Table 1. Vipulanandan curing model (Eqn. (4)) was used to predict the resistivity changes with the curing time for 28 days of curing as shown in Figure 4. The model predicted the experimental results very well. The model parameters p_1, q_1 and the ratio q_1/p_1 were all sensitive to the amount of NanoSiO$_2$ added to the cement.

Compressive Piezoresistivity and Strength of smart cement

Additional of about 0.1% carbon fibers substantially improved piezoresistive behavior of the cement and the electrical resistivity increased with the application of compressive loading, all new compared to the information in the literature [5, 6, 7, 8].

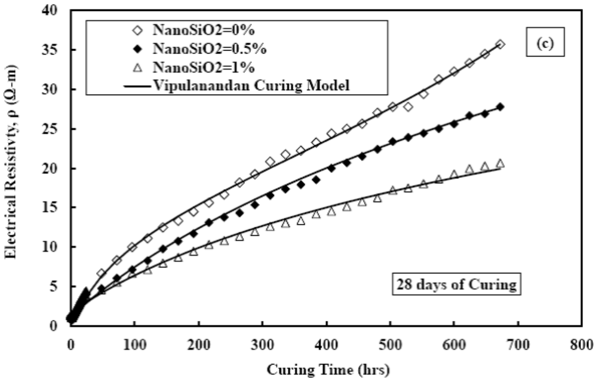


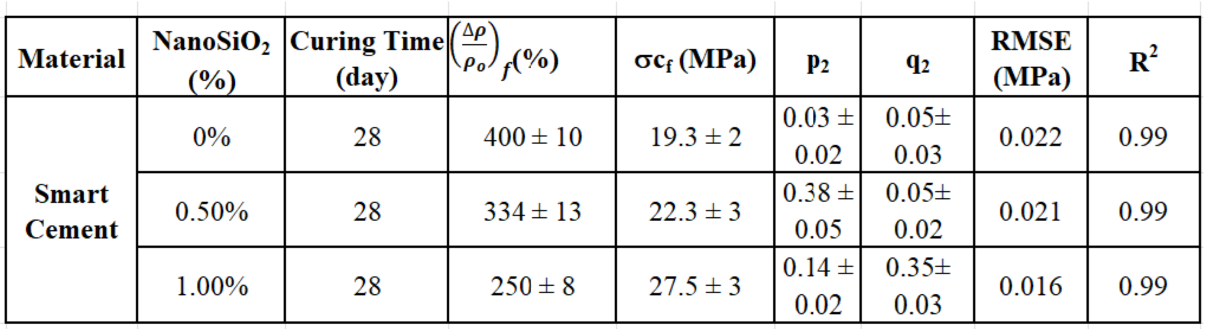
Figure 1: Curing of smart cement for 28 days curing with various amount of NanoSiO$_2$

Vipulanandan p-q piezoresistive model was used to predict the change in electrical resistivity of cement during with applied stress for 1, 7 and 28 days of curing. The Vipulanandan p-q piezoresistive model was defined as follows [4, 7, 8, 9]:

$$\frac{\sigma}{\sigma_f} = \left[\frac{\left(\frac{x}{x_f}\right)}{q_2 + (1 - p_2 - q_2)\frac{x}{x_f} + p_2\left(\frac{x}{x_f}\right)^{\frac{p_2}{p_2 - q_2}}} \right] \tag{5}$$

where σ:stress (psi); σ_f: stress at failure (psi); $x = (\frac{\Delta\rho}{\rho_o}) * 100$ = Percentage of change in electrical resistivity due to the stress; $x_f = (\frac{\Delta\rho}{\rho_o})_f * 100$ = Percentage of change in electrical resistivity at failure; $\Delta\rho$: change in electrical resistivity; ρ_o: Initial electrical resistivity (σ =0 MPa) and p_2 and q_2 are piezoresistive model parameters.

Table 2: Piezoresistive axial strain at failure and Strength of the Smart Cement without and with NanoSiO$_2$ After 28 days of Curing



Material	NanoSiO$_2$ (%)	Curing Time (day)	$\left(\frac{\Delta\rho}{\rho_o}\right)_f$(%)	σc_f (MPa)	p_2	q_2	RMSE (MPa)	R^2
Smart Cement	0%	28	400 ± 10	19.3 ± 2	0.03 ± 0.02	0.05± 0.03	0.022	0.99
	0.50%	28	334 ± 13	22.3 ± 3	0.38 ± 0.05	0.05± 0.02	0.021	0.99
	1.00%	28	250 ± 8	27.5 ± 3	0.14 ± 0.02	0.35± 0.03	0.016	0.99

28 days of Curing

Smart Cement

The piezoresistive axial strain of the smart cement at failure $\left(\frac{\Delta\rho}{\rho_o}\right)_f$ after 28 days of curing was 400%, as summarized in Table 2 and also shown in Figure 2. Compressive piezoresistive axial strain at failure reduced by 23% after 28 days of curing compared to the 7 days curing. The compressive axial failure strain was 0.22%, so the piezoresistive axial strain has been increased by 1,818 times (181,800%) making the smart cement to be highly sensing. The model parameters q_2 and p_2 were 0.05 and 0.03 respectively. The coefficient of determination (R^2) was 0.99 and the root-mean-square error (RMSE) was 0.022 MPa as summarized in Table 2.

Smart Cement with 0.5% NanSiO$_2$

The piezoresisitive axial strain of the smart cement with 0.5% NanoSiO$_2$ at failure $\left(\frac{\Delta\rho}{\rho_o}\right)_f$ after 28 days of curing was 334%, as summarized in Table 2 and shown in Figure 2. Compressive piezoresistive axial strain at failure reduced by 32.5% after 28 days of curing compared to the 7 days curing and the percentage reduction was higher than the smart cement without NanoSiO$_2$. Addition of 0.5% NanoSiO$_2$ reduced the piezoresistive axial strain of smart cement by 16.5%. The compressive axial failure strain was 0.20%, so the piezoresistive axial strain has been increased by 1,670 times (167,000%) making the smart cement to be highly sensing. The model parameters q_2 and p_2 were 0.05 and 0.38 respectively. The coefficient of determination (R^2) was 0.99 and the root-mean-square error (RMSE) was 0.021 MPa as summarized in Table 2.

Smart Cement with 1% NanSiO$_2$

The piezoresisitive axial strain of the smart cement with 1% NanoSiO$_2$ at failure $\left(\frac{\Delta\rho}{\rho_o}\right)_f$ after 28 days of curing was 250%, as summarized in Table 2 and shown in Figure 2. Compressive piezoresistive axial strain at failure reduced by 41.6% after 28 days of curing compared to the 7 days curing and the percentage reduction was higher than the smart cement without NanoSiO$_2$. Addition of 1% NanoSiO$_2$ reduced the piezoresistive axial strain of smart cement by 37.5%. The compressive axial failure strain was 0.19%, so the piezoresistive axial strain has been increased by 1,316 times (131,600%) making the smart cement to be highly sensing. The model parameters q_2 and p_2 were 0.35 and 0.14 respectively. The coefficient of determination (R^2) was 0.99 and the root-mean-square error (RMSE) was 0.016 MPa as summarized in Table 2.

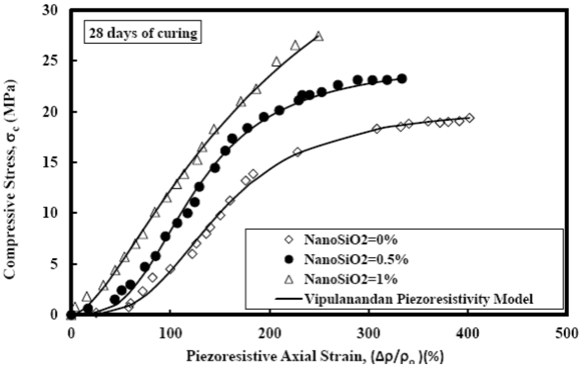


Figure 2: Compressive Piezoresistive behavior of smart cement with various amount of $NanoSiO_2$ after 28 days of curing.

Compressive Strength – Resistivity Index Relationship

During the entire cement hydration process both the electrical resistivity and compressive strength of the cement increased gradually with the curing time. For cement pastes with various $NanoSiO_2$ content, the change in the resistivity varied during the hardening. The cement paste without $NanoSiO_2$ had the highest electrical resistivity change (RI_{24hr}), as summarized in Table 1. The linear relationships between (RI_{24hr}) and the 1 day, 7 days and 28 days compressive strengths (MPa) as shown in Figure 3 are as follows:

$$\sigma_{1day} = -7 \times RI_{24\text{hr}} + 4066 \quad R^2 = 0.96 \quad (6)$$

$$\sigma_{7day} = -0.16 \times RI_{24\text{hr}} + 73 \quad R^2 = 0.90 \quad (7)$$

$$\sigma_{28day} = -0.05 \times RI_{24\text{hr}} + 28 \quad R^2 = 0.93 \quad (8)$$

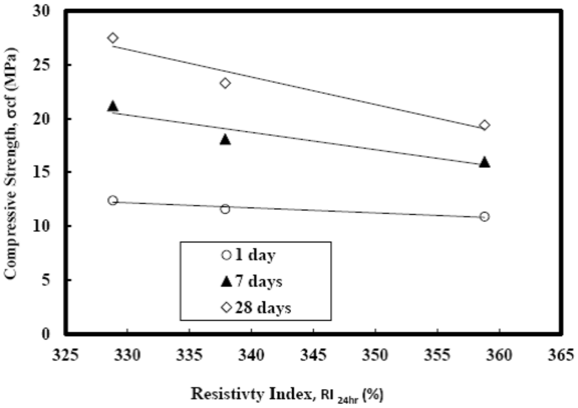


Figure 3: Relationship between resistivity index($RI_{24\text{ hr}}$) and compressive strength of smart cement modified with $NanoSiO_2$

Conclusions

Based on the experimental and analytical study on the smart cement modified with silica nanoparticles ($NanoSiO_2$) up to 1%, the following conclusions are advanced:

1. Resistivity was sensitive to the amount of $NanoSiO_2$ used to modify the smart cement. The amount of $NanoSiO_2$ can be detected based on the change in the initial resistivity. An addition of 1% $NanoSiO_2$ increased the initial electrical resistivity (ρ_o) of smart cement by 35% and also increased the time to reach minimum resistivity by 31 minutes. Initial electrical resistivity can be used as a good indicator for quality control. Vipulanandan p-q curing model predicted the behaviour very well.

2. Addition of 1% $NanoSiO_2$ increased the compressive strength of the smart cement by 14% and 42% after 1 day and 28 days of curing respectively. Also, the modulus of elasticity of the smart cement increased

with the additional of 1% $NanoSiO_2$. Vipulanandan p-q stress-strain model predicted the behaviour very well.

3. Addition of the $NanoSiO_2$ reduced the piezoresistivity (change the resistivity at peak stress) of the smart cement.Vipulanandan p-q piezoresistive model predicted the behaviour very well.
4. Linear correlations were found between resistivity index (RI_{24}) and compressive strength at different curing ages. Nonlinear model was used to correlate the model parameter to the curing time and $NanoSiO_2$ contents.

Acknowledgments

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