

# Effect of the Temperature on the Strength of Nanoclay-Based Cement under Geologic Carbon Sequestration

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## Abstract

Cement paste is known to react with CO<sub>2</sub>-saturated brine. Alteration of the cement properties is highly affected by the reservoir conditions. Nanoclay particles are recently suggested to mix with class G cement to enhance the strength of the cement matrix under geologic carbon sequestration. In this study, the effect of the reservoir temperature on the carbonation process of modified montmorillonite nanoclay-based cement will be studied.

Cement samples with and without modified montmorillonite nanoclay particles were cured for 24 hours, after that moved to CO<sub>2</sub> reactor and immersed into CO<sub>2</sub>-saturated brine at 1450 psi and two different temperature conditions of 95°C and 130°C for 30 days. The compressive and tensile strengths, porosity, and permeability of the cement samples were evaluated before and after reaction with the acidic brine.

The samples including nanoclay particles were able to withstand the retrogression in both compressive and tensile strengths after reacting with the acidic brine at 95°C and 130°C more than the base cement because of the pore-filling effect of the nanoclay particles. The strength of the base cement considerably decreased with the increase in the temperature, incorporating nanoclay particles improved the cement retrogression resistance with the increase in the temperature. After 30 days of reaction at 130°C, the compressive and tensile strengths of the base cement were decreased by 55.5% and 36.8%, respectively, compared with a decrease of 17.6% and 19.2% for the compressive and tensile strengths of the nanoclay-based cement.

## Introduction

Geologic carbon sequestration (GCS) is considered as a promising alternative to mitigate CO<sub>2</sub> escape into the atmosphere. It has also been used for a long time as an effective enhanced oil recovery (EOR) technique to enhance recovery of light and heavy oil (Picha et al. 2007; Ifeanyichukwu et al., 2014; Fath and Pouranfard, 2014; Huang et al., 2017).

Wang et al. (2013), Luo et al. (2014), and Zunsheng et al. (2014) evaluated the challenges and opportunities of the integrated EOR using CO<sub>2</sub> flooding with GCS in Ordos basin which is the second largest sedimentary basin in China. Ordos Basin is considered as the largest anthropogenic CO<sub>2</sub> emission

source in China because of the rapid development of the fossil energy-related industries in that area. As a result of the reservoir characterization and the simulation studies of CO<sub>2</sub> flooding Wang et al. (2013), Luo et al. (2014), and Zunsheng et al. (2014) concluded that integrating CO<sub>2</sub> EOR with GCS is an effective possible way to mitigate CO<sub>2</sub> emission in the region.

The possibility of sequestering CO<sub>2</sub> and simultaneously improve methane recovery for the purpose of enhanced gas recovery (EGR) applications was also evaluated by several studies such as Khan et al. (2013), Narinesingh and Alexander (2014), and Shi et al. (2017). The simulation results of all these studies confirmed the effectiveness of injecting CO<sub>2</sub> to recover methane and at the same time reduce CO<sub>2</sub> emission.

Risks of CO<sub>2</sub> escape from the geologic storage or the abundant reservoir is always there and the most possible pathways for such escape are through the cement body and the interfaces between the cement/formation and the casing/cement (Duguid et al., 2011; Zhang and Bachu, 2011; Iyer et al., 2017; Bagheri et al., 2018). Escape of CO<sub>2</sub> from the storage formation is caused by dissolution of the injected CO<sub>2</sub> into the brine which fills in the pore spaces of the storage formations, this dissolution leads to formation of carbonic acid that can then react with the cement sheath, and thus, change its composition, increase its porosity and permeability, and significantly decrease its strength (Kutchko et al., 2008; Kutchko et al., 2009; Duguid et al., 2011; Carey et al., 2010; Li et al., 2015a). The flow of CO<sub>2</sub> back to the atmosphere or to other formations containing potable groundwater through the damaged cement matrix could finally lead to safety concerns regarding the applications of GCS (Bachu and Bennion 2009; Connell et al., 2015).

Duguid and Scherer (2010) evaluated the degradation process of class H oil well cement under GCS conditions of 20°C to 50°C temperature and pH of 2.4 to 5 under flowing conditions. They reported that the degraded layers from outside of the core toward the center consist of a leached zone, a layer saturated with calcium carbonate, a layer depleted of calcium hydroxide, and the inside intact core which did not experience any carbonated brine attack. The presence of these four layers is also confirmed later by Li et al. (2015a) and Li et al. (2015b). Duguid and Scherer (2010) reported that the effect of increasing the temperature by 30°C (from 20°C to 50°C) considerably affected the cement degradation rate compared to the effect of increasing the pH by 1.3 units.

In a recent study by Mahmoud et al. (2018a) they evaluated the use of modified montmorillonite nanoclay (NC) particles on improving glass G oil well cement carbonation resistance under GCS conditions of 95°C and 1450 psi. Out of this study, the authors reported that adding 1.0% BWOC of NC improved the carbonation resistance of class G cement and they attributed this to the ability of the NC particles to accelerate the cement hydration process and formation of more stable forms of CSH products compared with the neat cement.

Another study by Mahmoud et al. (2018b) confirmed the ability to use the modified montmorillonite NC particles to improve the strength of class G oil well cement at very high-temperature and high-pressure (HPHT) conditions of 300°C and 3000 psi which usually encountered in the geothermal and high-temperature wells.

In this study, we will evaluate the effect of the temperature on the modified montmorillonite NC-based cement carbonation resistance under GCS conditions of 1450 psi and two temperature conditions of 95°C and 130°C.

## Experimental Program

This section summarizes the experimental procedures followed to accomplish this study. In the first part the materials used and the procedures of slurry preparation are explained, the second part summarizes the experiments conducted and the specifications of the samples used for every experiment.

## Materials

**Cement slurries.** The cement slurries used in this study were prepared using class G oil well cement, silica flour, friction reducer, expandable agent, fluid loss additive, defoamer, modified montmorillonite NC, and water. Class G oil well cement and all other additives are provided by a service company. The slurries were prepared according to the API procedures (API, 1991). Table 1 summarizes the composition of the cement slurries prepared for this study, both slurries have the same concentration of the different additives except the NC concentration where sample NC0 which is considered as the base slurry does not contain NC particles while sample NC1 contains 1.0% BWOC of the NC particles.

Table 1: The cement slurries composition.

Component	Additives Concentration	
	NC0	NC1
Cement (g)	600	600
Silica Flour (%BWOC)	35	35
Friction Reducer (%BWOC)	0.8	0.8
Expandable Agent (%BWOC)	1.0	1.0
Fluid Loss Additive (%BWOC)	0.75	0.75
Defoamer (%BWOC)	4.7E-07	4.7E-07
Water (%BWOC)	44	44
Nanoclay Particles (%BWOC)	0	1

## Methodology

After preparation of the cement slurries, they were poured into different metallic molds with different dimensions based

on the targeted test as will be elaborated in the next paragraphs. Half of the samples were then cured at 95°C and the other half is cured at 130°C, both samples cured at a pressure of 1450 psi. After 24 hours of hydration, the samples were then removed from the curing chamber and tested for their original compressive and tensile strengths, permeability, and porosity after that they were immersed into CO<sub>2</sub>-rich brine using the reaction chamber in Figure 1 and allowed to react with the acidic brine at a pressure of 1450 psi and temperatures of 95°C and 130°C for 30 days. The samples were then removed from the reaction vessel and tested for the change in their different properties again to compare the effect of the temperature on the carbonation resistance of the NC-based cement.

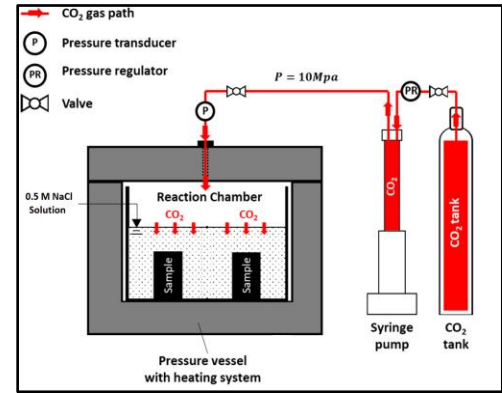


Figure 1. Schematic of the Reaction Chamber.

**Compressive strength measurements.** The compressive strength of the samples was evaluated based on the API standard (API, 2013) using cubical samples with dimensions of 2" by 2" by 2". The compressive strength evaluated at every condition using three cement cubes and then the compressive strength of the cement at that specific condition is calculated as the average strength of the three cubes.

**Tensile strength measurements.** The tensile strength of the cement samples is evaluated using cylindrical samples with 0.9" in length and 1.5" in diameter. The tensile strength at every condition was evaluated using three cylindrical cement samples and then the tensile strength of the cement at that specific condition is calculated as the average tensile strength of the three cylinders. The indirect tensile strength was determined by measuring the maximum load the sample could withstand before falling under tension. Then Eq. 1 was used to calculate the tensile strength of the sample.

$$\sigma_t = \frac{2P}{\pi dl} \quad \text{Eq. 1}$$

Where  $\sigma_t$  denotes the Brazilian tensile strength in (MPa),  $P$  is the failure load in (N),  $d$  and  $l$  are the cement sample diameter and length, respectively, both are in (mm).

**Permeability measurements.** The permeability of the cement

samples was measured on cylindrical samples of 0.5" in length and 1.5" in diameter. The permeability was measured using nitrogen gas as the measuring fluid.

**Porosity measurements.** The cement samples porosity was measured on cylindrical samples of 0.5" in length and 1.5" in diameter. The porosity was measured using helium gas as the measuring fluid.

## Results and Discussion

In this study, after preparing the cement slurries and being cured for 24 hours at a pressure of 1450 psi and temperatures of 95°C and 130°C, the compressive and tensile strengths, permeability, and porosity of the samples were evaluated before reaction with the CO<sub>2</sub>-saturated brine and after 30 days of carbonation inside the CO<sub>2</sub>-saturated brine at the same curing conditions. This section of the paper discusses the changes in the compressive and tensile strengths, permeability, and porosity of the samples as a result of carbonation at different temperature conditions.

### Compressive Strength

Figure 2 shows the compressive strength alteration for the cement samples before and after carbonation at 95°C and 130°C. Samples NC0 and NC1 have compressive strengths of 8768 and 10082 psi, respectively, before reaction with the acidic brine. When the samples immersed into the acidic brine for 30 days at 95°C their compressive strengths considerably decrease to reach 4764 psi (45.7% decrease) for sample NC0 and 9219 psi (8.6% decrease) for sample NC1. Reaction of samples NC0 and NC1 with the acidic brine for 30 days at 130°C decreased their compressive strengths by 55.5% and 17.6%, respectively, compared to their strengths before reaction with the CO<sub>2</sub>-saturated brine, the final strengths of samples NC0 and NC1 after reaction with the acidic brine at 130°C for 30 days are 3899 and 8303 psi, respectively.

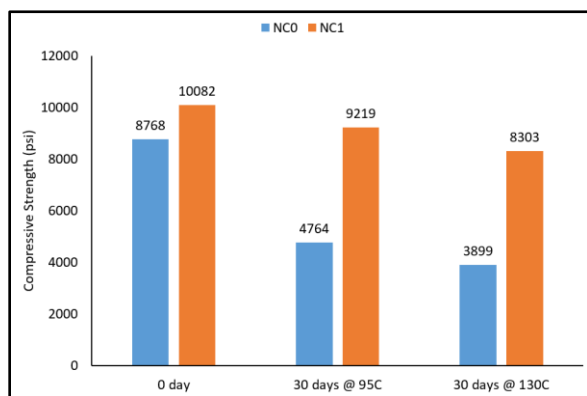


Figure 2. The compressive strength changes for samples NC0 and NC1 as a function of the carbonation time and temperature.

The decrease in the compressive strength of the samples containing NC particles is less than that of the cement without NC particles, this is attributed to the formation a densified

cement matrix and the pore-filling effects of the NC particles as will be confirmed later by the permeability and porosity measurement.

### Tensile Strength

The tensile strength measurements for the cement samples before and after reaction with the acidic brine as a function of time and temperature are summarized in Figure 3. As shown in this figure, the original tensile strengths of samples NC0 and NC1 are 729 and 806, respectively. The tensile strengths of samples NC0 and NC1 decreased by 27.3% and 9.8%, respectively, when reacted with the acidic brine at 95°C. The reaction of the cement samples NC0 and NC1 with the acidic brine at 130°C for 30 days decreased their tensile strengths by 36.8% and 19.2% compared to their initial strengths, respectively. The decrease in the tensile strengths of the samples containing NC is less than that of the base cement samples, and this is also attributed to the formation a densified cement matrix and the pore-filling effects of the NC particles.

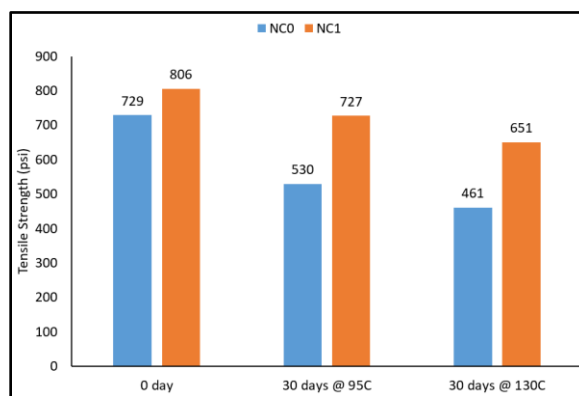


Figure 3. The tensile strength changes for samples NC0 and NC1 as a function of the carbonation time and temperature.

### Permeability

Figure 4 compares the permeability change before and after carbonation at 95°C and 130°C. Before the cement carbonation reaction, the cement samples NC0 and NC1 have permeabilities of 0.004 and 0.002 mD, respectively. Subjecting the cement samples to the carbonic acid at 95°C for 30 days increased the permeabilities of samples NC0 and NC1 to 0.006 and 0.003 mD, respectively. With an increase of 50% in both samples permeabilities prior to the carbonation reaction. When the samples are subjected to the high-temperature condition of 130°C the permeabilities of the samples were considerably increased, sample NC0 permeability is 0.022 mD and sample NC1 permeability is 0.010 mD as shown in Figure 4. All permeability measurements indicate that at the same conditions the NC-based cement samples have considerably less permeability compared with the base cement, these results confirmed the pore-filling effect of the nanoclay particles and formation of a densified cement matrix by incorporating nanoclay particles.

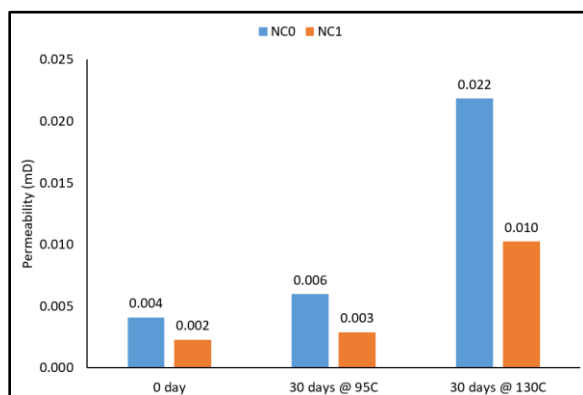


Figure 4. The permeability changes for samples NC0 and NC1 as a function of the carbonation time and temperature.

### Porosity

Figure 5 compares the change in the porosity of the cement samples at the different conditions considered in this study. The initial porosities of samples NC0 and NC1 are 27.3% and 23.1%, respectively. Porosity of sample NC0 increased to 31.5% and 34.1% when reacted at 95°C and 130°C, respectively, compared to the change in the porosity of sample NC1 which increased to 25.1% and 25.8%, respectively, after reacting with the acidic brine at 95°C and 130°C. The porosities of sample NC0 increased by 15.4% and 24.9% while these of sample NC1 increased by only 8.7% and 11.7% when reacted with the CO<sub>2</sub>-saturated brine at 95°C and 130°C.

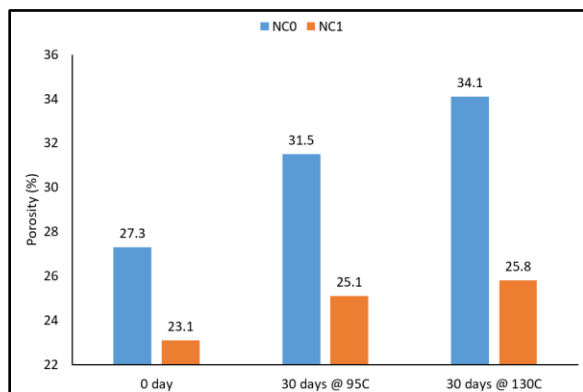


Figure 5. The porosity changes for samples NC0 and NC1 as a function of the carbonation time and temperature.

### Conclusions

In this study, the effect of the temperature conditions on the base and nanoclay-based cement undergoes carbonation reaction with CO<sub>2</sub>-saturated brine at 95°C and 130°C for 30 days was studied. The effect of the reaction temperature on the compressive and tensile strengths, permeability, and porosity of the cement samples was evaluated and the following points are concluded:

- The base cement samples (i.e the samples without nanoclay) compressive and tensile strengths decreased by 45.7% and 27.3%, respectively, when reacted with the

acidic brine at 95°C, and by 55.5% and 36.8%, respectively, when reacted at 130°C.

- The decrease in the compressive and tensile strengths of the base sample was decreased by incorporating 1% BWOC of modified montmorillonite nanoclay particles.
- The compressive and tensile strengths of the samples incorporating nanoclay were decreased by only 17.6% and 19.2% at a high-temperature of 130°C.
- The ability of the nanoclay particles to reduce the decline in the cement compressive and tensile strengths is attributed to the ability of the nanoclay particles to fill the pore spaces of the cement and produce a densified cement matrix as indicated by porosity and permeability measurements.
- The initial permeability of the cement was reduced from 0.004 to 0.002 mD, with a reduction rate of 50% by incorporating 1% BWOC of NC.
- The base cement samples permeability increased to 0.022mD compared to 0.01 mD for the samples including 1% BWOC of nanoclay when the samples are reacted at 130°C.
- The porosity of the base and nanoclay-based samples reacted at 130°C increased by 24.9% and 11.7%, respectively, compared with their initial porosities.

### Nomenclature

API	= American Petroleum Institute
BWOC	= By Weight of Cement
EGR	= Enhanced Gas Recovery
EOR	= Enhanced Oil Recovery
GCS	= Geologic Carbon Sequestration
HPHT	= High-Pressure and High-Temperature
NC	= Nanoclay

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