Structural evolution in Nanoclay reinforced oilwell cement during Supercritical CO₂ (ScCO₂) invasion

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Abstracts. Supercritical CO₂ (ScCO₂) invades oilwell cement and forms carbonate layers in the cement under geological CO2 sequestration conditions. Long-term invasion of ScCO₂ makes the carbonation structure unstable and prone to damage. Nanoclay was modified with ScCO₂ as the solvent and intercalator for the reinforcement of oilwell cement, forming the microcrystalline Nanoclay (MC Nanoclay). MC Nanoclay is identified and added into the cement slurry to reinforce oilwell cement after the above modification. Microcrystal calcite is found in the MC Nanoclay with transmission electron microscopy (TEM) and selected area electron diffraction (SAED) analyses. Both mechanical properties and microstructural evolution of MC Nanoclay reinforced oilwell cement are investigated, showing that the carbonation was inhibited with MC Nanoclay. With generalized analysis from microcrystal formation and densified carbonation area, the reinforce mechanisms of MC Nanoclay were revealed in this study.

Keywords:
Nanoclay; Supercritical CO₂; Oilwell cement; Structure evolution
1. Introduction
Since the 1970s and 1980s, CO₂ capture and injection projects have been operated for enhanced oil recovery (EOR)[1,2]. Large-scale commercial carbon capture, utilization and storage (CCUS) has been proposed to control the Greenhouse effects. Climate targets and substantial investments make great efforts on CCUS technology to build a net-zero emission energy system for the earth [3]. To achieve the net-zero goal world widely, supercritical CO₂ (ScCO₂, CO₂ above the critical temperature and pressure) was considered the most efficient fluid and sequestered in the formations through the injection wells. As a crucial material, the oilwell cement is exposed to the ScCO₂ condition underground and keeps the CO₂ injection wells sealed well for decades [4–6]. Although, previous researches have revealed the carbonation reactions of cement at various conditions. The high solubility, low viscosity, and low surface tension of ScCO₂ result in the accelerated deconstruction of the cement matrix and severe damage to the CO₂ injection wellbore [7–9]. Thus, it still needs further study in the reinforcement methods and structure evolutions for the oilwell cement when ScCO₂ invaded it.

As a natural and popularly used material, Nanoclay has been attached importance again in many other applications. Due to the layer structure capacity and accessibility, Nanoclay can be modified with organic and inorganic agents [10,11]. Based on the previous works, it is possible to embed the functional compositions with economical methods [12]. Apart from the composition modifications of Nanoclay, microcrystallization of Nanoclay is supposed to promote the reactive property and would be a promising and low-cost industrialization method for large-scale utilization [13–16]. In our study, to improve the ScCO₂ utilization, Nanoclay can modify ScCO₂ and investigate the modification reactions. To clarify the reinforcement of modified Nanoclay, oilwell cement mixed with modified Nanoclay was evaluated based on the structure evolution in the ScCO₂ conditions.

2. Methodology

2.1 Experimental
Nanoclay powder used in this study was less than 1μm in particle size. The Nanoclay powder was modified by the ScCO₂ (8.0 MPa and 62 °C) in a high-pressure reactor for 24 hours. After the ScCO₂ modification, the powder was oven-dried in room condition isolated from the environment to stabilize the composition and structure. The modified Nanoclay was named the MC Nanoclay.

Oilwell cement samples investigated in this topic were prepared according to the API RP-10B[17] criterion. The mixture ratio of these samples was as Table 1 shown.

| Table 1. Compositions and mixture ratio |
|----------------------------------------|
| Compositions | G-class oilwell cement | Water | Dispersant | Water reducer | Nanoclay or MC Nanoclay |
| Wt %         | 100.00               | 44.00 | 1.50       | 2.00          | 2.00                    |

Sample IDs were NC and MC, respectively, corresponding to samples prepared with Nanoclay and MC Nanoclay. The curing parameters of the studied samples were 17.0 MPa,
62 °C and 1.00 wt % NaCl brine according to the CO₂ sequestration well condition for 14 days[18]. After 14 days of curing, experimental samples were exposed to the ScCO₂ condition at 8.0 MPa, 62 °C and 100% CO₂ for 7, 14 and 28 days. The sample size for different characterizations was different. The mechanism samples were prepared according to the criterion above mentioned. CT scanning samples were prepared in tubes with Φ10 × 20 mm cylinders. All these samples were cured and exposed to the ScCO₂ under the same conditions.

2.2 Characterizations
Different methods were utilized in this study to characterize the Nanoclay powder and the oilwell cement stones. Morphology changes of Nanoclay and MC Nanoclay were scanned by the TEM (Transmission Electron Microscope, JEOL JEM-2100F, Japan), and crystal structure analysis was tested with the SAED (Selected Area Electron Diffraction, TEM equipped). According to the API RP-10B, as for the oilwell cement samples with different Nanoclay powders, compressive strength was tested by the electronic hydraulic testing machine (RMT-150C, Institute of Rock and Soil Mechanics, China). Cement samples were scanned before and after exposure to ScCO₂ with the μ-CT (μ X-ray computed tomography, Zeiss Xradia 410 Versa μ-CT machine, Germany), according to the parameters of 80 kV, 125 μA, and exposure time is 2 s.

3. Results

3.1 Composition analysis
As the previous studies revealed [14], after reacting with ScCO₂, Nanoclay phases produce microcrystalline phases. To directly identify the structure of the microcrystalline phase, the TEM images and SAED maps of the MC Nanoclay powders were presented in Figure 1. The Nanoclay powder is amorphous with agglomerates structure, and some fragmented phase surrounds the amorphous phases in Figure 1. With agglomerates reduction, some trigonal crystals were seen in the images. Similar to the results reported in previous studies [19,20], the SAED image in Figure 1 was mainly composed of (104), (012), (110), and (113), which suggested this crystal was nanoscale calcite. The TEM image (Figure 1) exhibited the corresponding planes in the trigonal crystal with d-spacing about 0.385, 0.303, 0.249, and 0.228 nm, which indicated that the trigonal crystal was the nanoscale calcite. Dispersion of agglomerates can increase the adsorbing capacity of Nanoclay during the ScCO₂ modification.
3.2 Mechanics properties
Mechanics properties directly presented the structure changes due to reaction with CO₂. Unlike the carbonation of CO₂ gas or solutions, the ScCO₂ has much better permeability and fluidity. As Figure 2 shows, after 14 days of curing, the mechanics of the MC samples are a little lower than the NC samples, with 38.71 MPa and 41.85 MPa, respectively. As the ScCO₂ invasion, the compressive strength was decreased dramatically in both NC and MC samples. Compared to the control samples, the NC07 and MC07 were 68.07% and 64.86% relative compressive strength left. It should be noted that the compressive strength of NC samples keeps decreasing during 28 days of ScCO₂ invasion, with only 24.59 MPa. Therefore, the Nanoclay without modification cannot stop the ScCO₂ from permeating into and changing the oilwell cement matrix. Although MC samples show a lower value than NC samples at the first 7 days, the compressive strength of MC28 increases to 28.04 MPa. Moreover, the compressive strength of MC28 has regained the 72.43% of control samples. MC Nanoclay should contribute to the reinforcement proceeding in oilwell cement during long-term ScCO₂ invasion.
Figure 2. Compressive strength of NC and MC samples after exposure in the \( \text{ScCO}_2 \).

3.3 Structural analysis

The CT images were post-processed by Avizo 2020 to obtain inner structures of samples. The probability distribution maps (PDMs) and area ratio of structures were adopted to understand the structure and phase evolution among the NC and MC samples during \( \text{ScCO}_2 \) invasion. PDMs can present the structure and phase evolution in qualitative results. Comparing with the MC14, the carbonation area in the NC14 sample was significantly increased to 23.93%, which made the structure unstable and resulted in the continuous reduction of compressive strength. Different from the NC14 case, a minor change of carbonation and more cement matrix left in MC14 led to regained strength. Ultimately, when the \( \text{ScCO}_2 \) invasion lasted for 28 days, the dissolution area of the Nanoclay sample increased to 3.64% from 1.05% in NC14. In contrast, the dissolution area of MC28 decreased to 1.90% from 3.98%. The cement matrix in MC28 remained at 75.16%, which was higher than the case in NC28 (about 68.49%). Therefore, it is interesting to notice that the compressive strength of MC28 regained 72.43% of the unexposed samples in Figure 2. Therefore, the MC Nanoclay was able to change the structural evolution during \( \text{ScCO}_2 \) invasion into the oilwell cement.
4. Discussion

The CO$_2$ inhibition mechanism of MC Nanoclay was shown in Figure 4. Firstly, considering the dissolution reactions [21,22], the released Ca-ions can be captured by the MC Nanoclay to make the compositions chemically rebalance. Secondly, the calcite microcrystals can induce carbonates deposition and make a densified carbonation layer [23,24], which can seal the dissolution area as the PDMs shown in Figure 3. The compressive strength regains in MC samples benefited from MC Nanoclay coupling mechanisms during ScCO$_2$ invasion in the oilwell cement.

Figure 3. Probability distribution maps of structures and components in NC and MC samples during ScCO$_2$ invasion.
5. Conclusion
In this study, a novel method for modification of Nanoclay was proposed using ScCO$_2$. The phases, morphological structures, and the adsorption capacity of Nanoclay were investigated before and after the modification. The TEM and SEAD results revealed that microcrystal calcites were formed during the carbonation reaction of the Nanoclay. The adsorption capacity tested by TGA proved the effectiveness of the CO$_2$ adsorption in the Nanoclay when the ScCO$_2$ functioned as the modification medium. Using numerous CT images obtained and related processing algorithms, the carbonation area was quantitatively estimated, and the structural evolution was presented with the PDMs. With the identification results of MC Nanoclay, it can be implied that the reinforcement mechanism of MC Nanoclay was primarily due to montmorillonite swelling and microcrystalline calcite-induced carbonates formation.

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