



# Evaluation of CO<sub>2</sub> attack in wellbore class G cement: influence of epoxy resins, composites and minerals as additives

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**Abstract:** Carbon dioxide (CO<sub>2</sub>) injection into geological formations is pointed out as one of the most effective alternatives to reduce anthropogenic CO<sub>2</sub> emissions to the atmosphere. To promote long-term CO<sub>2</sub> storage, wellbore integrity is a critical issue to be considered. Portland cement is commonly used for cementing wells, and considered chemically unstable in CO<sub>2</sub>-rich media. In this context, this study investigated the CO<sub>2</sub> chemical resistance of class G Portland cement modified with novel additives (epoxy resins, epoxy–clay composites, and clay minerals) at 1 and 2.5 wt% contents. Reaction times of 7 and 30 days of exposure to CO<sub>2</sub> in supercritical conditions were evaluated. Samples were characterized by mechanical compression tests and phenolphthalein indicator as well as field emission scanning electron microscopy in order to determine the depth of carbonation in cement. Our results indicate that although there is slight reduction in the initial compressive strength, the addition of tested additives to cement paste offers improvements in terms of chemical resistance. The optimum content of different additives was 1 wt% in order to maintain compressive strength properties and improve chemical resistance to CO<sub>2</sub>. The best result was achieved with an epoxy resin blend as an additive, decreasing carbonation by up to 60% (7 days of exposure to CO<sub>2</sub>) and 52% (30 days of exposure to CO<sub>2</sub>). Addition of montmorillonite to the epoxy blend tends to improve chemical resistance of cement

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paste when compared to the neat epoxy blend. © 2019 Society of Chemical Industry and John Wiley & Sons, Ltd.

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## Introduction

In order to strengthen the global response to climate change threat, the Paris Agreement was signed in 2015 with targets for countries to maintain the average temperature rise below 2°C compared to preindustrial levels. The Fifth Assessment Report of the Intergovernmental Panel on Climate Change (Working Group III – IPCC)<sup>1</sup> points out that large-scale changes in energy systems over the coming decades will be essential to reduce carbon dioxide (CO<sub>2</sub>) levels in the atmosphere.<sup>1–5</sup> In this scenario, CO<sub>2</sub> capture and storage is indicated as one of the alternatives to reduce fossil carbon emission.<sup>1,6</sup>

Successful long-term storage operation is highly dependent on the safety injection of CO<sub>2</sub> under supercritical conditions with no occurrence of leakages.<sup>7–11</sup> Portland cement is the most common material applied in oil and gas wells construction to create a barrier in order to prevent leakages and fluid flow between geological formations in wellbore zones.<sup>8</sup> Davies *et al.*<sup>12</sup> point out that about 7% of abandoned wells in the world (over 26 000 wells) have some types of integrity failure. Cement quality and casing corrosion are the main problems related to wellbore integrity. Such failures can lead to significant environmental impacts such as gas leakage into the atmosphere as well as water and soil contamination.<sup>7,10,13</sup>

To predict potential CO<sub>2</sub> leakage from wellbores, it is crucial to understand transfer phenomena and chemical reactions between CO<sub>2</sub> and well materials.<sup>8,14</sup> Chemical reactions are the most common concerns related with wellbore integrity due to the instability of Portland cement in CO<sub>2</sub>-rich aqueous environments and many geochemical reactions that occur continuously during the cement degradation process such as cement components dissolution (e.g., calcium and silicon oxides), reaction products precipitation (calcium carbonates), and casing corrosion. In this scenario, sealing efficiency of the cement depends on environmental conditions as well as chemical composition and additives present in the cement paste (cement and water mixture).

In terms of cement degradation, when CO<sub>2</sub> is in contact with formation, water produces carbonic acid (H<sub>2</sub>CO<sub>3</sub>) that alters the chemical behavior of cement. H<sub>2</sub>CO<sub>3</sub> diffuses into the cement matrix and changes the medium's pH, reacting with calcium hydroxide (Ca(OH)<sub>2</sub>) and calcium silicate hydrate (CSH). These reactions can lead to physical changes such as porosity and permeability increase, promoting zonal isolation loss and gas migration.<sup>7,15–18</sup> Reaction kinetic rates between cement components and CO<sub>2</sub> are fast and driven by the reaction equilibrium rates.<sup>19</sup> Cement paste behavior depends significantly on the products resulting from these reactions.

Several studies have shown that addition of different types of additives (e.g., polymeric, nano and inorganic materials) can improve cement chemical and mechanical properties.<sup>20–27</sup> Genedy *et al.*<sup>26</sup> studied epoxy cement nanocomposites incorporating nanosilica, nanoclay, and nanoalumina as repair materials for wellbores. Incorporation of silica and alumina significantly improved bond strength with both steel and cement compared to standard cement. Besides, the epoxy nanocomposites have acceptable flowability that enables injection in wellbore cracks. Childers *et al.*<sup>27</sup> combined disulfide containing epoxies with wellbore cements to produce thermally stable self-healable polymer–cement composites. Such composites exhibit rheological properties comparable to the standard cement as well as high compressive strength. With regard to this mechanical property, reduction in compressive resistance is found for the polymer–cement composites compared to the standard cement. However, compressive strengths are still high and above the requirements for geothermal well cementing. Despite significant advancement in the development of cementitious materials for wellbore applications, there are very few studies on the evaluation of chemical resistance of modified cement pastes in CO<sub>2</sub>-rich environments and under wellbore conditions.<sup>28–32</sup> Previous studies from our research group have shown that degradation by CO<sub>2</sub> of class G cement paste can be reduced using polymeric materials as additives.<sup>28–30</sup> Baldissera *et al.*<sup>29</sup> evaluated the chemical resistance of cement paste under wellbore

**Table 1. Chemical composition and density of class G cement.**

Composition	%
SiO <sub>2</sub>	21.25
Al <sub>2</sub> O <sub>3</sub>	3.95
Fe <sub>2</sub> O <sub>3</sub>	4.57
CaO	65.07
MgO	2.31
SO <sub>3</sub>	2.27
Na <sub>2</sub> O	0.25
K <sub>2</sub> O	0.33
Density (g·cm <sup>-3</sup> )	3.1

conditions by adding different epoxy resins at various contents (5–50%). The results showed that the addition of epoxy resin up to 30% can improve the chemical resistance of cement paste exposed to CO<sub>2</sub> for 7 days. In addition to epoxy resins, studies using a blend of epoxy resins reinforced with mineral fillers (agalmatolite, talc, and montmorillonite) have shown promising results, reducing the degradation of cement paste by CO<sub>2</sub>.<sup>28</sup> Schütz *et al.*<sup>28</sup> showed that cement paste modified with the composite containing montmorillonite had the lower degraded layer (897 and 751 μm with 2.5% and 5% of composite) compared to unmodified cement paste (1192 μm), representing an improvement of 25% and 37%, respectively, on the chemical resistance against CO<sub>2</sub> attack. Long-term experiments are still necessary and could help to predict the performance of epoxy resins and epoxy–clay composites as additives for cement paste in CO<sub>2</sub> storage conditions.

Taking into account our previous results,<sup>28–30</sup> the main goal of this study was to evaluate the influence of low contents (1 and 2.5 wt%) of different additives on

the chemical resistance of class G cement paste over 7 and 30 days of exposure to CO<sub>2</sub> under wellbore conditions. Samples were prepared by adding the following additives to cement paste: (i) epoxy resin systems (pure and blend), (ii) an epoxy blend system reinforced with montmorillonite and talc (epoxy–clay composites), or (iii) only montmorillonite and talc minerals.

## Materials and methods

### Cement

Class G Portland cement from LafargeHolcim was used in this study. The cement chemical composition is shown in Table 1. The cement paste was prepared using a mixer according to American Petroleum Institute (API) Specification 10A<sup>33</sup> with a water/cement ratio of 0.44.

### Epoxy resin systems

Two bicomponent epoxy resin systems (Huntsman Corporation, Woodlands, TX), denominated as A and D, were used in this study. System A was prepared by mixing resin 1 (diglycidyl ether of bisphenol A) and hardener at 100:144 weight ratio; in contrast, system D was composed by an epoxy blend system (resins 1 and 2) and hardener at 80:20:144 weight ratio, as shown in Table 2. According to the supplier's information, the addition of epoxy resin 2 (phenol-Novolac) to resin 1 in the recommended proportion (80:20 wt%) can upgrade the performance offered by the epoxy resin 1. The hardener was mixed with the epoxy resins and the systems were kept at room temperature for 15 min for induction time. Such induction time is required in order to make the epoxy resins and hardener fully compatible. Epoxy resin systems (A and D) were added to cement paste at 1 and 2.5 wt% contents.

**Table 2. Properties of epoxy resins used in this study.**

Epoxy resin	Epoxy equivalent (g·eq <sup>-1</sup> )	Viscosity at 25°C (mPa·s)	Density at 25°C (g·cm <sup>-3</sup> )	Mix proportion (wt%) <sup>a</sup>
1	182–192	12 000–16 000	1.17	80
2	172–179	1100–1700	1.22	20
Hardener (waterborne amine)	–	–	1.08	144

<sup>a</sup>Recommended by the supplier (Huntsman Corporation).

**Table 3. Chemical composition and properties of clay minerals used in this study.**

Organoclay – MMT	
Organic modifier	Dimethyl, dihydrogenated tallow, quaternary ammonium
Modifier concentration	125 meq/100 g clay
Density	1.66 g·cm <sup>-3</sup>
Natural talc	
Quantification of mineral phases by XRD (%)	
Talc	54
Chlorite	19
Magnesite	1
Dolomite	3
Serpentinite	4

## Clay minerals

Two clay minerals were used as fillers to obtain the reinforced epoxy resin blends: (i) natural talc (Taltech Tecnologia em Minerios Ltda, Brazil) and (ii) organically modified montmorillonite – MMT (Southern Clay Products). Chemical composition and properties of the clay minerals are shown in Table 3. Taking into account literature data<sup>34–36</sup> in order to enhance mechanical properties and maintain processability of the epoxy resins, fixed content of 5 wt% of clay mineral was mixed with the epoxy blend system (system D), which is calculated with respect to the epoxy blend mass. Talc and MMT were also used to obtain samples of cement paste additivated only with clay minerals. For these samples, 1 and 2.5 wt% contents were added to the anhydrous cement.

## Sample preparation

For comparison purposes, unmodified cement paste (referred in this study as reference) was prepared according to API 10A,<sup>33</sup> as follows: water is poured into the mixer and stirred at 4000 rpm; then, the anhydrous cement is added, within not more than 15 s, while the mixer is operating at 4000 rpm, and the mixing speed is increased to 12 000 rpm for 35 seconds. Cement paste containing the epoxy resins (systems A and D) and the reinforced epoxy resin blends (MMT and talc as fillers) were prepared using the M2 method, as described elsewhere.<sup>28</sup> In this method, cement paste is prepared according to API 10A<sup>33</sup> and the mixer is turned off. The epoxy additives are added to the cement paste and stirred for additional 40 s at 12 000 rpm. Regarding the

samples containing only clay minerals (MMT and talc), the minerals were directly added to the anhydrous cement and then mixed with the water used for cement hydration according to API 10A.<sup>33</sup>

All samples were obtained using additives of 1 and 2.5 wt%, which are casted in cylindrical molds (10 mm diameter and 20 mm height) for thermal curing (thermostatic bath at 70°C) for over 14 days in order to keep the recommended minimum curing period for class G cement.<sup>37</sup> Moreover, the temperature applied in thermal curing aims to mimic wellbore conditions in a scenario of geological CO<sub>2</sub> storage.

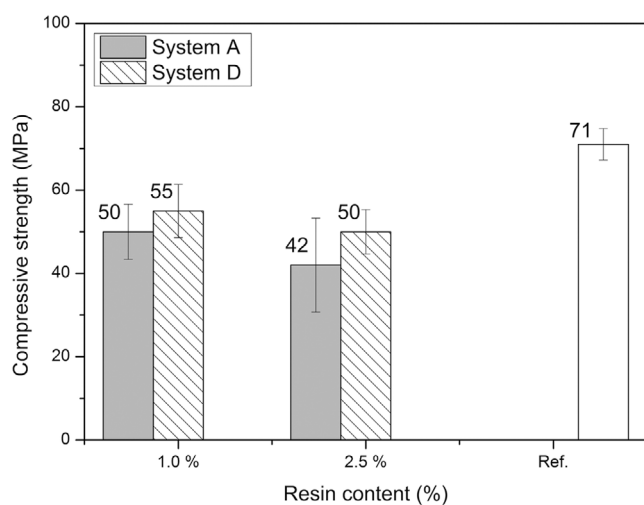
## CO<sub>2</sub> degradation experiments

Cured samples were exposed to water-saturated CO<sub>2</sub> at 70°C with constant CO<sub>2</sub> pressure of 50 bar (high purity, 99.9%, White Martins) for 7 and 30 days under static conditions in order to simulate realistic wellbore conditions after the CO<sub>2</sub> injection period.

## Characterization of uncarbonated and carbonated samples

Samples were characterized by phenolphthalein indicator, field emission scanning electron microscopy (FESEM), and mechanical compressive strength tests. For phenolphthalein tests, cylindrical samples were cut into half with a diamond cutting disc, and phenolphthalein solution (2% in ethyl alcohol–water, 48:50% v/v) was dripped on the newly exposed inner surface as a color indicator for the presence of Ca(OH)<sub>2</sub>. With this test, both nondegraded (pink colored) and degraded (not colored) layers can be identified in the carbonated samples, which is a quick and easy test for an initial assessment of carbonation. FESEM analyses were carried out with FEI Inspect F50 microscope at 10–20 kV. Such an analysis allows estimating accurately the thickness of the degraded layer by CO<sub>2</sub>. The thickness values are presented as a mean value of multiple points of analysis in the degraded area. Only uncarbonated cement paste samples were subjected to mechanical compression test in order to assess the effect of the addition of the different additives (epoxy resins and clay minerals) on the initial compressive strength of the cement. Specimens of 21 days (7-day experiments) and 44 days (30-day experiments) were used for initial compression tests in order to evaluate the same age for uncarbonated and carbonated samples after 14 days of thermal curing. Compressive strength was determined





**Figure 1.** Initial compressive strength for cement paste additivated with pure epoxy resin (system A) and epoxy resin blend (system D); and for unmodified cement paste (reference). Values are the mean and standard deviation for triplicate measurements ( $n = 3$ ).

according to ASTM C39<sup>38</sup> using Shimadzu 300 kN universal testing machine at a crosshead speed of  $1 \text{ mm} \cdot \text{min}^{-1}$  with cylindrical specimens (23 mm diameter and 46 mm height). The cylindrical specimens were fitted at the center in compression testing machine and a very small load was applied to keep the sample in position. The load was then slowly applied to the tested sample until to the sample's failure. The results of compressive strength testing are the mean for three replicates.

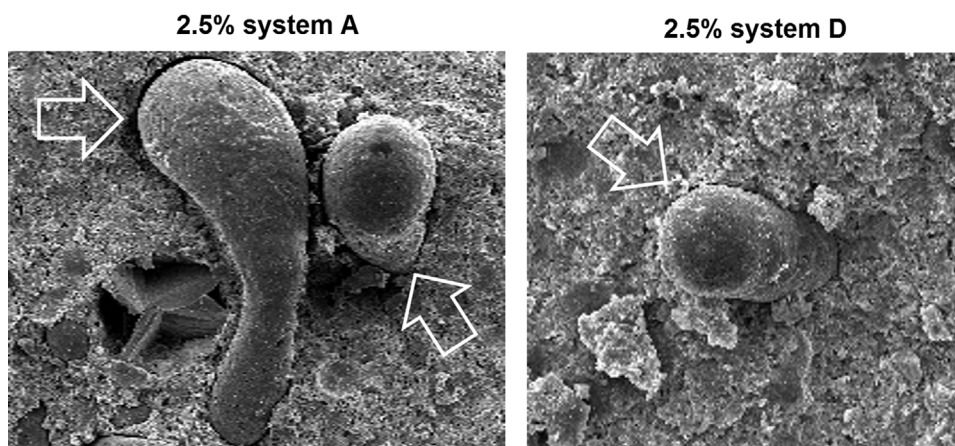
## Results and discussion

### Compressive strength of additivated cement paste

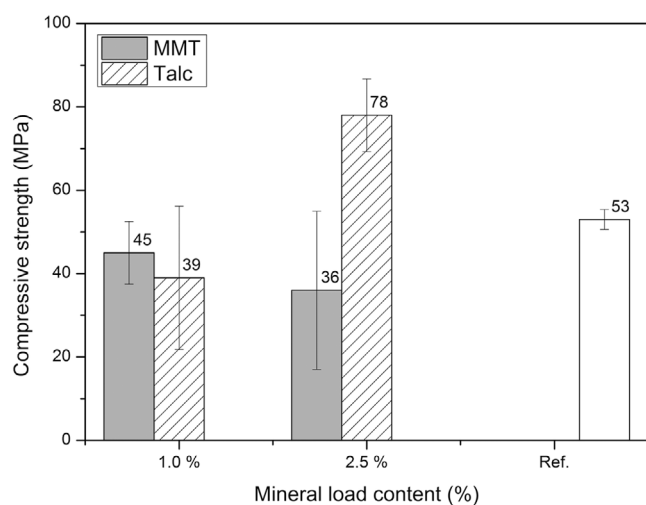
The initial compressive strength results of the cement paste additivated with pure epoxy resin (system A) and epoxy resin blend (system D) are shown in Fig. 1. These results were obtained for uncarbonated samples and are compared with the reference sample (Ref.).

The results indicate decrease in compressive strength for the samples additivated with systems A and D when compared with the reference. Comparing system A with system D for the same content (1% or 2.5%), system A leads to the maximum decrease in cement strength. Considering the average values of compressive strength, the decrease observed in system A was in the order of 29% and 41% for 1% and 2.5% contents, respectively; in contrast, in system D, a decrease of 22% and 29% was found in compressive strength at 1% and 2.5%, respectively.

By evaluating the additive content in the cement paste, both epoxy systems at 1% show less decrease in the compressive strength than at 2.5%. In addition, samples additivated with 1% of system D have the lowest decrease in compressive strength when compared to the reference. Childers *et al.*<sup>27</sup> have found similar results using epoxy resins as an additive in wellbore cement, observing a decrease in compressive strength with the increases in additive content in cement paste. Decreasing in compressive strength with the increases in epoxy resin content in the cement paste can be explained by the highest formation of



**Figure 2.** FESEM photomicrographs of the cement paste additivated with 2.5% pure epoxy resin (system A) and epoxy resin blend (system D), showing formation of polymer clumps (indicated by arrows) within the cement matrix.



**Figure 3.** Initial compressive strength for cement paste additivated with clay minerals (MMT and talc); and for unmodified cement paste (reference). Values are the mean and standard deviation for triplicate measurements ( $n = 3$ ).

polymer clumps within the cement matrix, which represents areas of stress concentration providing points of weakness in the structure<sup>28</sup> (Fig. 2). Figure 3 shows the effect of MMT and talc additives in the initial compressive strength of the cement paste.

According to Fig. 3, addition of MMT to cement paste promotes about 15% and 32% decrease in compressive strength, for 1% and 2.5% contents, respectively, when compared to the reference. With respect to talc, a decrease of 26% in strength is found at 1% contents. However, when cement paste was additivated with 2.5%, an increase of 47% in strength is observed. Studies have shown that talc-based cementitious materials exhibit an increase in compressive strength as the talc content increases in the material.<sup>39,40</sup> Talc is a hydrated layered magnesium silicate with chemical formula  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ . As the addition of such magnesium-rich mineral increases, an improvement in compressive strength can be expected due to chemical interactions between the mineral and the cement hydration products. Sudalaimani *et al.*<sup>40</sup> point out that portlandite ( $\text{Ca}(\text{OH})_2$ ) most probably reacts with magnesium that increases the content of brucite ( $\text{Mg}(\text{OH})_2$ ) in combination with reduction of portlandite — the very low solubility of brucite favors the consumption of  $\text{Ca}(\text{OH})_2$ . By increasing the content of magnesium-rich mineral in the cement, a denser microstructural bond is observed, which can contribute to the enhancement of compression strength. However, the authors stress out that the

percentage of magnesium-rich mineral should not exceed 20%; otherwise, a disintegrated microstructure is formed with the reduction in compression strength. In general, mineral additives can influence nucleation process in the early cement hydration, which affects the early strength and pozzolanic activity of the mineral.<sup>41,42</sup> By comparing the results shown in Figs 1 and 3, better performance of cement paste is achieved with 1% of epoxy resin systems (A and D) and clay minerals (MMT and talc), indicating an optimum content of additive in cement paste with respect to compression strength properties. It is noteworthy that despite the reduction in compressive strength for the additivated cement pastes (except for 2.5% talc), samples exhibit compressive strength performance higher than the minimum compressive strength performance required for class G cement, according to API 10A.<sup>33</sup>

### Additives effect on the cement chemical resistance: 7-day experiments

Cement degradation by CO<sub>2</sub> was evaluated by phenolphthalein indicator and degraded layer measurements obtained by FESEM. In Fig. 4, longitudinal sections are presented for the samples additivated with pure epoxy resin (system A), epoxy resin blend (system D), and reinforced epoxy resin blend (MMT and talc as filler) at 1% and 2.5% contents after 7- and 30-day carbonation. After phenolphthalein test, the presence of gray regions in the sample periphery is observed, indicating  $\text{Ca}(\text{OH})_2$  consumption for all samples.

According to Fig. 4, additivated samples exhibit smaller degraded layers than the reference for 7-day experiments, regardless of the epoxy content (1% or 2.5%) and the epoxy system (A or D). In addition, cement paste additivated with system D presents a lower extent of degradation than that with system A.

The average depths of the degraded layers from both epoxy systems were determined by FESEM (Fig. 5). The results confirm the phenolphthalein findings, indicating that samples additivated with epoxy resin blend (system D) exhibit higher chemical resistance to CO<sub>2</sub>. Cement paste additivated with pure epoxy resin (system A) exhibits a decrease in CO<sub>2</sub> degradation by 47% and 45% for 1% and 2.5% contents, respectively. When epoxy resin blend (system D) was used as an additive, a decrease of 60% and 62% in the degraded layer depth is found when compared to the reference.

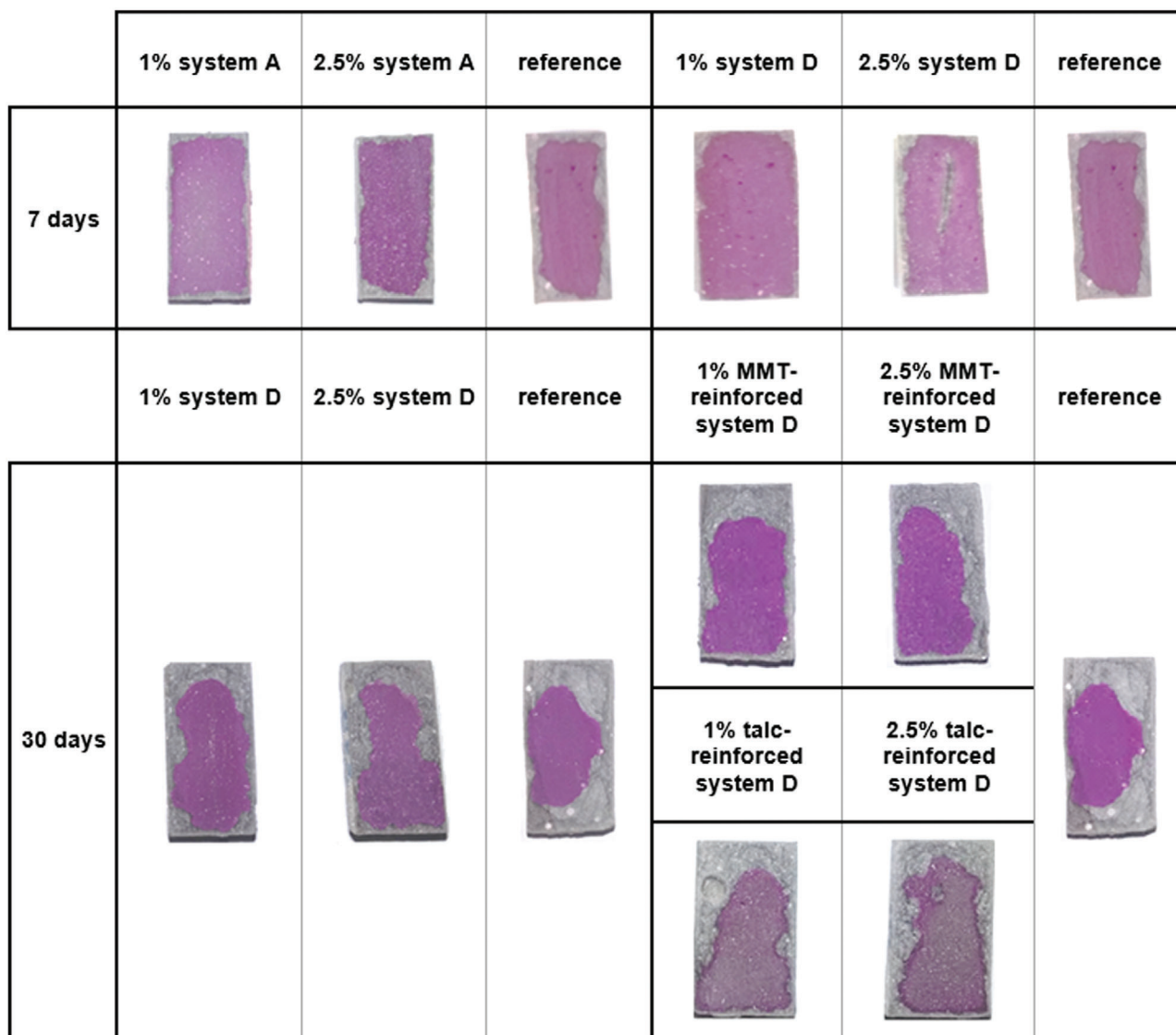


Figure 4. Phenolphthalein test for cement paste additivated with pure epoxy resin (system A), epoxy resin blend (system D), and reinforced epoxy resin blend (MMT and talc as filler); and for unmodified cement paste (reference); 7- and 30-day experiments.

As shown in Fig. 5, the degraded layer depth does not vary significantly considering 1% and 2.5% contents for the same additive (systems A and D). Such result indicates that the addition of 1% of additive is enough to reduce cement degradation by CO<sub>2</sub>. The average degraded layer value was in order of 680 μm for the samples additivated with system A and 500 μm with system D. Addition of both systems to cement paste leads to smaller degraded layers than those found in the reference (~1300 μm).

Degradation by CO<sub>2</sub> of samples additivated only with clay minerals (MMT and talc) was also evaluated in this study. Figure 6 presents the degraded layer

measurements obtained from FESEM after 7 days of exposure to CO<sub>2</sub>.

According to Fig. 6, MMT and talc at 1% content promote higher chemical resistance to CO<sub>2</sub> compared to the reference. Among all additivated samples, cement paste with 1% of talc exhibits the best performance (smaller degraded layer), showing an average degraded layer depth of 1034 μm. In terms of carbonation reduction, the addition of 1% of clay minerals promotes 28% and 42% of reduction for MMT and talc, respectively. When cement paste was additivated with 2.5% of MMT, the average degraded layer depth was 2179 μm, which is higher than the

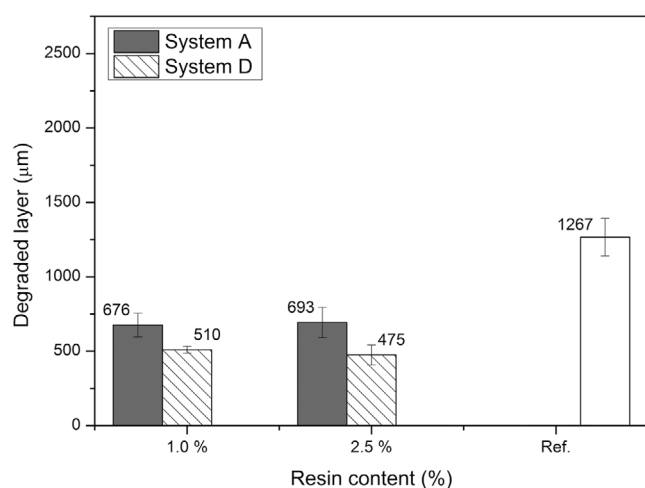


Figure 5. Thickness of the degraded layer for cement paste additivated with pure epoxy resin (system A) and epoxy resin blend (system D); and for unmodified cement paste (reference); 7-day experiments. Values are the mean and standard deviation for multiple measurements.

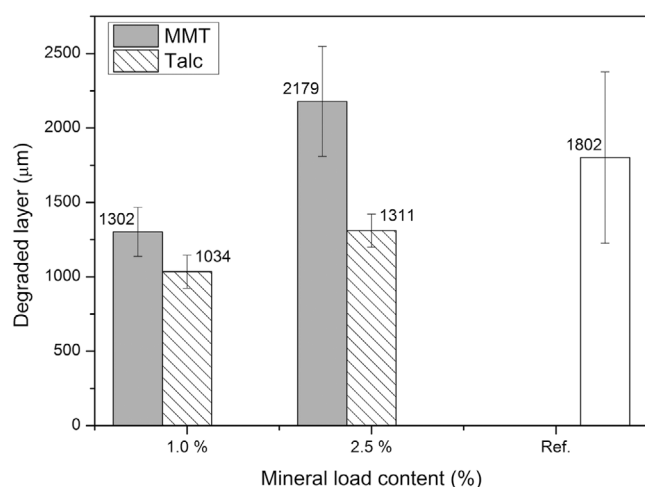


Figure 6. Thickness of the degraded layer for cement paste additivated with MMT and talc; and for unmodified cement paste (reference); 7-day experiments. Values are the mean and standard deviation for multiple measurements.

degraded layer depth measured in the reference (1801 µm). An increase of 21% in carbonation is observed for these samples when compared to reference. By adding 2.5% of talc to cement paste, an average degraded layer of 1311 µm is found, which is smaller than the reference and practically the same found with 1% of MMT (1034 µm). Cement paste additivated with 2.5% of talc exhibits a reduction of 27% in carbonation. In general, talc promotes better chemical resistance against CO<sub>2</sub> attack at all evaluated

contents. These findings are supported by Sudalaimani and Shanmugasundaram's work,<sup>40</sup> which suggests that the amount of Ca(OH)<sub>2</sub> is reduced in talc-based cementitious materials due to its reaction with magnesium from talc mineral. Therefore, carbonation reaction is expected to be diminished at low contents of portlandite.

### Additives effect on the cement chemical resistance: 30-day experiments

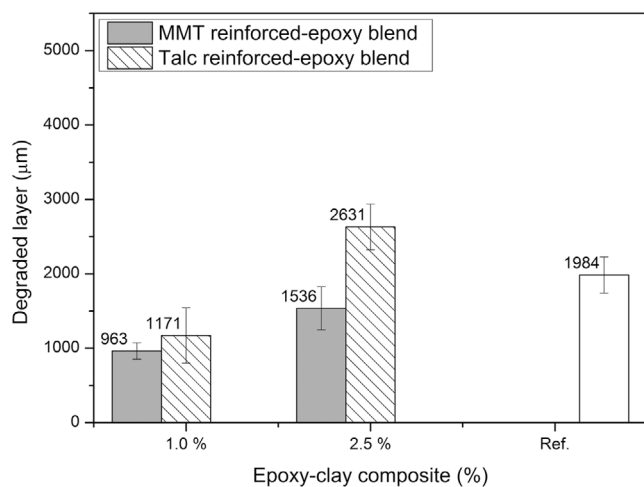
In order to evaluate the exposure time on the cement chemical resistance, CO<sub>2</sub> degradation experiments were carried out for 30 days with cement paste additivated with epoxy resin blend (system D), since this system showed the best results with respect to CO<sub>2</sub> resistance (Fig. 5). Note that a longer exposure time to CO<sub>2</sub> is more adequate for a real evaluation of performance of the tested additives in storage conditions.

According to Fig. 4, cement paste additivated with system D at 1% and 2.5% contents exhibits smaller degraded layer than that found in the reference. In addition, samples with 1% of system D tend to exhibit lower degradation than samples with 2.5% of system D. Therefore, the results shown in Fig. 4 indicate that the addition of an epoxy resin blend to cement paste improves the chemical resistance against CO<sub>2</sub> attack even after 30 days of exposure. By comparing the exposure time, a degraded layer less uniform is observed for the samples exposed to CO<sub>2</sub> during 30 days.

Confirming the phenolphthalein results, degraded layer measurements by FESEM show that cement paste additivated with 1% of system D has the best chemical resistance after 30-day exposure to CO<sub>2</sub>, showing an average degraded layer (1632 µm) smaller than the 2.5% additivated sample (1877 µm) and the reference (3376 µm). A reduction of 52% and 44% in carbonation is found for the samples additivated with 1% and 2.5% of system D, respectively.

In order to evaluate the synergistic effect of epoxy resin and clay mineral on the CO<sub>2</sub> resistance, cement paste was additivated with the epoxy blend system reinforced with MMT and talc (epoxy-clay composites) at 1% and 2.5% contents. Note that the content of clay mineral in the epoxy blend was kept constant at 5 wt%. According to Fig. 4, additivated cement paste exhibits higher chemical resistance than the reference. Among the additives, MMT-reinforced



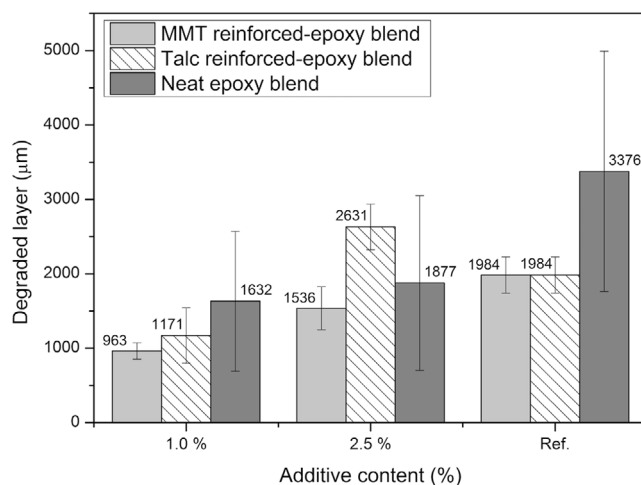


**Figure 7.** Thickness of the degraded layer for cement paste additivated with reinforced epoxy resin blend (MMT and talc as filler); and for unmodified cement paste (reference); 30-day experiments. Values are the mean and standard deviation for multiple measurements.

epoxy blend seems to decrease the degradation at a greater extent when compared to the talc-reinforced epoxy blend. Our previous studies pointed out that cement pastes additivated with epoxy–clay composites containing an organically modified MMT undergo lower degradation than those containing talc, most likely due to a better dispersion of the filler (clay mineral) within polymer matrix.<sup>28</sup> Although the talc-reinforced epoxy blend shows smaller degraded layer than the reference, the phenolphthalein test indicates leaching of components into cement core due to the color difference in the pink area when compared to the samples additivated with MMT-reinforced epoxy blend (strong pink in cement core).

According to Fig. 7, the best results are achieved with 1% reinforced epoxy blend regardless of the filler (MMT or talc). Cement paste additivated with 1% of MMT-reinforced epoxy blend exhibits a decrease of 52% in degradation, whereas talc-reinforced epoxy blend exhibits a decrease of 41%. By adding 2.5% of epoxy–clay composite, only the cement paste additivated with MMT exhibits satisfactory chemical resistance, showing a decrease of 22% in degradation when compared to the reference.

Regarding the epoxy–clay composites, results show that the synergistic effect of resin and clay mineral can improve CO<sub>2</sub> resistance of the cement paste after 30 days of carbonation. By comparing the samples additivated with neat epoxy resin blend (system D) and



**Figure 8.** Thickness of the degraded layer for cement paste additivated with neat epoxy blend (system D); reinforced epoxy resin blend (MMT and talc as filler); and for unmodified cement paste (reference); 30-day experiments. Values are the mean and standard deviation for multiple measurements.

samples additivated with epoxy–clay composites (Fig. 8), smaller degraded layers are found for cement paste additivated with epoxy–clay composites with best results at 1% contents: 963 µm for MMT-reinforced epoxy blend; 1171 µm for talc-reinforced epoxy blend; and 1632 µm for system D (neat epoxy blend). Cement paste additivated with MMT-reinforced epoxy blend has smaller degraded layer at 1% (963 µm) and 2.5% (1536 µm) in comparison to the neat epoxy blend (1632 µm and 1877 µm, respectively) as well as to the talc-reinforced epoxy blend (1171 µm and 2631 µm, respectively), showing that addition of MMT to epoxy blend promotes a higher CO<sub>2</sub> resistance for cement paste when compared to talc mineral. As shown in Fig. 6, cement paste additivated only with talc has smaller degraded layer at 1% (1034 µm) and 2.5% (1311 µm) contents than cement paste additivated with talc-reinforced epoxy blend.

## Conclusions

Novel additives for class G Portland cement paste were investigated in order to improve its chemical resistance under common conditions encountered in deep CO<sub>2</sub> disposal. Our results show that a low additive content (1 wt%) is sufficient to promote a significant increase in chemical resistance without considerable loss of compressive strength properties. By comparing the two epoxy resin systems (A and D) as additives, a decrease

in CO<sub>2</sub> degradation by 47% and 60% is found for cement paste containing system A and D, respectively, at 1% content and after 7 days of exposure to CO<sub>2</sub>. Successful performance of system D (an epoxy resin blend) is maintained even after 30 days of carbonation, exhibiting a reduction in carbonation of 52% when compared to the reference (unmodified cement paste). Regarding the clay minerals (MMT and talc), cement paste additivated only with talc exhibits greater chemical resistance, reducing carbonation by 42% at 1% content and after 7 days of carbonation, whereas MMT reduces carbonation by 28%. However, when the epoxy resin blend is reinforced with the clay minerals (epoxy–clay composites), the results show that 1% and 2.5% of MMT-reinforced epoxy blend promotes better chemical resistance to cement paste than talc-reinforced epoxy blend. After 30 days, a decrease in carbonation by 52% and 22%, at 1% and 2.5% contents, respectively, is found for cement paste additivated with MMT-reinforced epoxy blend. By comparing the cement paste additivated with epoxy resin blend and with epoxy–clay composites, the results show that the addition of MMT to epoxy blend tends to promote greater CO<sub>2</sub> resistance for cement paste in comparison to the talc-reinforced epoxy blend and the neat epoxy blend. This study provides promising additives to be applied to Portland cement in CO<sub>2</sub>-rich media, aiming to ensure wellbore integrity and promote safety long-term CO<sub>2</sub> storage.

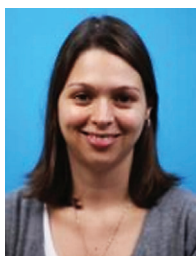
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## References

- Intergovernmental Panel on Climate Change. *Climate Change 2014: Mitigation of Climate Change: Working Group III Contribution to the IPCC Fifth Assessment Report. Working Group III Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* (2014). Intergovernmental Panel on Climate Change. <https://doi.org/10.1017/CBO9781107415416>
- Ghezloun A, Saidane A and Merabet H, The COP 22 new commitments in support of the Paris Agreement. *Energy Procedia* **119**:10–16 (2017).
- Bataille C, Åhman M, Neuhoff K, Nilsson LJ, Fishedick M, Lechtenböhmer S *et al.*, A review of technology and policy deep decarbonization pathway options for making energy-intensive industry production consistent with the Paris Agreement. *J Clean Prod* **187**:960–973 (2018).
- Dong C, Dong X, Jiang Q, Dong K and Liu G, What is the probability of achieving the carbon dioxide emission targets of the Paris Agreement? Evidence from the top ten emitters. *Sci Total Environ* **622–623**:1294–1303 (2018).
- Millar RJ, Fuglestedt JS, Friedlingstein P, Rogelj J, Grubb MJ, Matthews HD *et al.*, Emission budgets and pathways consistent with limiting warming to 1.5°C. *Nat Geosci* **10**:741–747 (2017).
- Kemper J, Biomass and carbon dioxide capture and storage: a review. *Int J Greenh Gas Control* **40**:401–430 (2015).
- Kiran R, Teodoriu C, Dadmohammadi Y and Nygaard R, Journal of Natural Gas Science and Engineering identification and evaluation of well integrity and causes of failure of well integrity barriers (a review). *J Nat Gas Sci Eng* **45**:511–526 (2017).
- Shen J, Dangla P and Thiery M, Reactive transport modeling of CO<sub>2</sub> through cementitious materials under supercritical boundary conditions, in *Geomechanics in CO<sub>2</sub> Storage Facilities*, ed. by Pijaudier-Cabot G and Pereira J-M. John Wiley & Sons, Hoboken, NJ, pp. 181–208 (2013).
- Iyer J, Walsh SDC, Hao Y and Carroll SA, Assessment of two-phase flow on the chemical alteration and sealing of leakage pathways in cemented wellbores. *Int J Greenh Gas Control* **69**:72–80 (2018).
- Boothroyd IM, Almond S, Qassim SM, Worrall F and Davies RJ, Science of the total environment fugitive emissions of methane from abandoned, decommissioned oil and gas wells. *Sci Total Environ* **547**:461–469 (2016).
- Cunningham AB, Gerlach R, Spangler L, Mitchell AC, Parks S, Phillips A *et al.*, Reducing the risk of well bore leakage of CO<sub>2</sub> using engineered biomineralization barriers. *Energy Procedia* **4**:5178–5185 (2011).
- Davies RJ, Almond S, Ward RS, Jackson RB, Adams C, Worrall F *et al.*, Oil and gas wells and their integrity: implications for shale and unconventional resource exploitation. *Mar Pet Geol* **56**:239–254 (2014).
- Sminchak JR, Moody M, Gupta N and Larsen G, Wellbore integrity factors for CO<sub>2</sub> storage in oil and gas producing areas in the Midwest United States. *Greenh Gases Sci Technol* **7**:817–827 (2017).
- Liu S, Li D, Yuan J, Qi F, Shen J, Guo M *et al.*, Cement sheath integrity of shale gas wells: a case study from the Sichuan Basin. *Nat Gas Ind B* **5**:22–28 (2018).
- Rimmelé G, Barlet-Gouédard V, Porcherie O, Goffé B and Brunet F, Heterogeneous porosity distribution in Portland cement exposed to CO<sub>2</sub>-rich fluids. *Cem Concr Res* **38**:1038–1048 (2008).
- Walsh SDC, Du Frane WL, Mason HE and Carroll SA, Permeability of wellbore-cement fractures following degradation by carbonated brine. *Rock Mech Rock Eng* **46**:455–464 (2013).
- Hernández-Rodríguez A, Montegrossi G, Huet B, Vaselli O and Virgili G, A study of wellbore cement alteration controlled by CO<sub>2</sub> leakage in a natural analogue for geological CO<sub>2</sub> storage. *Appl Geochem* **86**:13–25 (2017).
- Liaudat J, Martínez A, López CM and Carol I, Modelling acid attack of oilwell cement exposed to carbonated brine. *Int J Greenh Gas Control* **68**:191–202 (2018).
- Lesti M, Tiemeyer C and Plank J, CO<sub>2</sub> stability of Portland cement based well cementing systems for use on carbon capture & storage (CCS) wells. *Cem Concr Res* **45**:45–54 (2013).

20. Ohama Y, *Handbook of Polymer-Modified Concrete and Mortars: Properties and Process Technology*. William Andrew, Norwich, NY (1995).
21. Mangadlao JD, Cao P and Advincula RC, Smart cements and cement additives for oil and gas operations. *J Pet Sci Eng* **129**:63–76 (2015).
22. Yang Y, Yuan B, Wang Y, Zhang S and Zhu L, Carbonation resistance cement for CO<sub>2</sub> storage and injection wells. *J Pet Sci Eng* **146**:883–889 (2016).
23. Hussein KM, Bouchra EH, El Youbi MS and Ahmed E, Development and study of physical, chemical and mechanical properties of a new formulation of cement of a varying percentage of natural Pozzolan. *J Chem Technol Metall* **52**:873–884 (2017).
24. Bu Y, Chang Z, Du J and Liu D, Experimental study on the thermal expansion property and mechanical performance of oil well cement with carbonaceous admixtures. *RSC Adv* **7**:29240–29254 (2017).
25. Cheng XW, Khorami M, Shi Y, Liu KQ, Guo XY, Austin S, Saidani M *et al.*, A new approach to improve mechanical properties and durability of low-density oil well cement composite reinforced by cellulose fibres in microstructural scale. *Constr Build Mater* **177**:499–510 (2018).
26. Genedy M, Stormont J, Matteo E and Taha MR, Examining epoxy-based nanocomposites in wellbore seal repair for effective CO<sub>2</sub> sequestration. *Energy Procedia* **63**:5798–5807 (2014).
27. Childers MI, Nguyen M-T, Rod KA, Koech PK, Um W, Chun J *et al.*, Polymer-cement composites with self-healing ability for geothermal and fossil energy applications. *Chem Mater* **29**:4708–4718 (2017).
28. Schütz MK. *et al.*, Chemical degradation of reinforced epoxy-cement composites under CO<sub>2</sub>-rich environments. *Polym Compos* **39**:E2234–E2244 (2018).
29. Baldissera AF, Schütz MK, Santos LD, Vecchia FD, Seferin M, Ligabue R *et al.*, Epoxy resin-cement paste composite for wellbores: evaluation of chemical degradation fostered carbon dioxide. *Greenh Gases Sci Technol* **7**:1065–1079 (2017).
30. Baldissera AF, Schütz MK, Vecchia FD, Seferin M, Ligabue R, Menezes S *et al.*, Epoxy-modified Portland cement: effect of the resin hardener on the chemical degradation by carbon dioxide. *Energy Procedia* **114**:5256–5265 (2017).
31. Nasvi MCM, Ranjith PG and Sanjayan J, Effect of different mix compositions on apparent carbon dioxide (CO<sub>2</sub>) permeability of geopolymers: suitability as well cement for CO<sub>2</sub> sequestration wells. *Appl Energy* **114**:939–948 (2014).
32. Xu B, Yuan B, Wang Y, Zeng S and Yang Y, Nanosilica-latex reduction carbonation-induced degradation in cement of CO<sub>2</sub> geological storage wells. *J Nat Gas Sci Eng* **65**, 237–247 (2019).
33. API Specification 10A, *Specification for Cements and Materials for Well Cementing*, 23rd Edition. API, Washington, DC (2002).
34. Komarneni S, Feature article. Nanocomposites. *J Mater Chem* **2**:1219 (1992).
35. Ho MW, Lam CK, Lau Kak, Ng DHL and Hui D, Mechanical properties of epoxy-based composites using nanoclays. *Compos Struct* **75**:415–421 (2006).
36. Azeez AA, Rhee KY, Park SJ and Hui D, Epoxy clay nanocomposites – processing, properties and applications: a review. *Compos Part B Eng* **45**:308–320 (2013).
37. ASTM C150, *Standard Specification for Portland Cement*. ASTM International, West Conshohocken, PA (2011).
38. ASTM C39, *Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens*. ASTM International, West Conshohocken, PA (2014).
39. Ngally Sabouang CJ, Mbey JA, Liboum Thomas F and Njopwouo D, Talc as raw material for cementitious products formulation. *J Asian Ceram Soc* **2**:263–267 (2014).
40. Sudalaimani K and Shanmugasundaram M, Influence of ultrafine natural steatite powder on setting time and strength development of cement. *Adv Mater Sci Eng* **2014**:1–6 (2014).
41. Laibao L, Yunsheng Z, Wenhua Z, Zhiyong L and Lihua Z, Investigating the influence of basalt as mineral admixture on hydration and microstructure formation mechanism of cement. *Constr Build Mater* **48**:434–440 (2013).
42. Saraya ME-SI, Study physico-chemical properties of blended cements containing fixed amount of silica fume, blast furnace slag, basalt and limestone, a comparative study. *Constr Build Mater* **72**:104–112 (2014).



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