Organic acid concentration thresholds for ageing of carbonate minerals: implications for CO₂ trapping/storage

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Highlights:

- Carbonate aquifers (Calcite Surfaces)
- Dissolution of organic acid components in crude oil (Stearic Acid)
- CO₂ trapping in deep saline aquifers and depleted hydrocarbon reservoirs and their associated risk in the presence of organic acid components

Keywords:

Wettability, CO₂ storage, Organic acids
Abstract

Hypothesis: CO₂ geological storage (CGS) involves different mechanisms which can store millions of tonnes of CO₂ per year into depleted hydrocarbon reservoirs and deep saline aquifers. But their storage capacity is influenced by the presence of different carboxylic compounds in the reservoir. These molecules strongly affect the water wetness of the rock, which has a dramatic impact on storage capacities and containment security. However, precise understanding of how these carboxylic acids influence the rock’s CO₂-wettability is lacking.

Experiments: We thus systematically analysed these relationships as a function of pressure, temperature, storage depth and organic acid concentrations. A particular focus was on identifying organic acid concentration thresholds above which storage efficiency may get influenced significantly.

Findings: These thresholds (defined for structural trapping as a water contact angle θ > 90°; and for capillary trapping when primary drainage is unaffected, i.e. θ > 50°) were very low for structural trapping (~10⁻³ – 10⁻⁷ M organic acid concentration C_organic) and extremely low for capillary trapping (10⁻⁷ M to below 10⁻¹⁰ M C_organic). Since minute organic acid concentrations are always present in deep saline aquifers and certainly in depleted hydrocarbon reservoirs, significantly lower storage capacities and containment security than previously thought can be predicted in carbonate reservoirs, and reservoir-scale models and evaluation schemes need to account for these effects to de-risk CGS projects.

1. Introduction

Depleted hydrocarbon reservoirs and deep saline aquifers are potential CO₂ sinks in which anthropogenic CO₂ emissions can be stored, thus mitigating global warming.¹,² Efficient and safe CO₂ geological storage involves a qualitative and quantitative assessment of the
contribution of the different functional trapping mechanisms which prevent the buoyant CO$_2$
from migrating back to the surface.[1]

In this context it has been shown that CO$_2$-wet surfaces drastically reduce structural$^{[3-5]}$ and
capillary trapping capacities.$^{[6-9]}$ Furthermore, it is clear that organic acid content on the rock
surface is the main factor which renders (originally strongly water-wet) mineral surfaces to
become CO$_2$-wet.$^{[4]}$ While clean mineral surfaces are weakly, strongly or completely water-
wat,$^{[10-13]}$ organic acid surfaces, e.g. alkylated or arylated minerals, minerals aged in crude oil
or coal$^{[4,5,14,15]}$ are weakly, strongly or even completely CO$_2$-wet depending on pressure,
temperature and brine salinity.$^{[4,16,17]}$

However, chemically clean mineral surfaces are artificial in the sense that they can only be
prepared and persist in strongly oxidising environments (e.g. in oxygen plasma or in UV-ozone
atmosphere).$^{[18,19]}$ while it is well established that in the subsurface anoxic or reducing
conditions prevail.$^{[20,21]}$

In addition, it is clear that storage formations always contains traces of dissolved organic acid
material,$^{[22-27]}$ which is potentially sufficient to significantly change the rock’s CO$_2$-wettability.
Indeed a partial mono-molecular layer adsorbed to the mineral surface would be sufficient for
this.$^{[19,28-33]}$ Such organic acid contaminations thus has the potential to drastically reduce
storage capacities and containment security.$^{[5,9,34,35]}$ It is therefore of vital importance to gauge
this effect and to identify threshold concentrations of organic acid molecules at which CO$_2$
storage is significantly affected.

We thus systematically investigated such threshold values per clearly defined laboratory
experiments; and we analysed the impact such minute organic acid concentrations have on CO$_2$
storage capacities and containment security.
2. Experimental Methodology

2.1. Materials

Nine pure calcite samples (Iceland spar, from WARD’S Natural Science, sample dimensions \(= 1 \text{ cm} \times 1 \text{ cm} \times 0.3 \text{ cm}\)) were used as a model limestone storage formation. The surface roughnesses of all nine surfaces were measured via Atomic Forces Microscopy (AFM instrument model DSE 95-200, Semilab).

\(\text{CO}_2\) (purity = 99.999 mol%; from BOC, gas code-082), \(\text{N}_2\) (purity = 99.999 mol%; from BOC, gas code-234) and 10 wt% NaCl brine (NaCl purity \(\geq 99.9\) mol%; from Scharlab) were used. The NaCl was dissolved in deionized water (Ultrapure from David Gray; electrical conductivity = 0.02 mS/cm), which was equilibrated with calcite by rigorously mixing with calcite off-cuts while continuously monitoring the pH value.\(^{[36,37]}\) Subsequently the NaCl brine was equilibrated with \(\text{CO}_2\) at experimental conditions in a high pressure mixing reactor.\(^{[38]}\)

Acetone (99.9 mol%; from Rowe Scientific) was used as surface cleaning agent, drops of hydrochloric acid (ACS reagent, concentration 37 vol%, Sigma Aldrich) were used to control the pH of the brine (see ageing procedure below for more details) and stearic acid (\(\geq 98.5\) mol%; from Sigma Aldrich) was selected as a model for organic acid molecules present in the subsurface.\(^{[25,39-42]}\)

2.2. Simulating real aquifer conditions

As mentioned above, real aquifers contain organic acid molecules which are partially adsorbed on the rock surface.\(^{[22-27]}\) It is thus vital to re-create such mineral surfaces to realistically mimic aquifer rock surfaces, particularly with respect to their wettability characteristics.\(^{[28,43-45]}\) Thus below the procedure for preparing such realistic aquifer surfaces is described, as it was used in this research work.
2.2.1 Calcite surface preparation

Initially the mineral (calcite) substrates were cleaned with calcite-equilibrated DI-water to remove any dust or surface fragments from the surface. The sample was then dried in an oven at 90°C for 60 mins and exposed to air plasma (using a Diemer Yocto instrument) for 15 mins to remove any organic contamination.[18,19]

Ageing procedure

To mimic a typical storage formation, where the rock pore surfaces were exposed to formation water over geological times,[40-50] we adopted the following strategy:

The calcite samples were immersed for 30 mins in calcite-equilibrated 2 wt% NaCl brine (NaCl purity ≥ 99.9 mol%; from Scharlab) at ambient conditions, while the acidity was maintained at pH = 4 by adding drops of aqueous hydrochloric acid; this procedure increases the adsorption rate of stearic acid onto the substrate, and thus simulates adsorption of organic acid molecules over geological times (i.e. millions of years exposure time).[40-50] Ultraclean N₂ was then used to mechanically clean (blow away) the remaining water from the surface to avoid contamination. Subsequently the substrates were aged in stearic acid/n-decane solutions of prescribed molarity (10⁻² M to 10⁻¹⁰ M stearic acid concentration) for seven days to mimic exposure to formation fluid (which contains organic acid molecules) over geological times.[39,40,51,52] Note that it is also shown that carboxylic acids and hydrocarbons both exist in deep saline aquifers,[53], as a result of biodegradation and organic matter diagenesis and subsequent migration into the water zones.[54]

Mechanistically, the stearic acid esterifies the hydroxyl groups on the calcite surface in a condensation reaction (Scheme 1).[55-59]
Scheme 1. Chemisorption of stearic acid (CH\(_3\)(CH\(_2\))\(_{16}\)-COOH) on solid calcite surface (\(\wedge\) indicates solid bulk).\(^{[55-59]}\)

Thus octadecanoate groups (C\(_{18}\) ester groups) were chemically (covalently) bonded to the calcite surface, rendering them strongly hydrophobic.\(^{[60]}\)

### 2.2.2. Surface characterization of pure and aged calcite surfaces

**Pure calcite**

The surface properties of the calcite samples were investigated via energy dispersive X-ray spectroscopy (EDS, Oxford X-act SSD X-ray detector with Inca and Aztec software), atomic force microscopy (AFM DSE 95-200, Semilab) and contact angle (\(\theta\)) measurements. For pure calcite surfaces, the average atomic surface content was 24.7 wt% ± 4.9 wt% Ca, 20.5 wt% ± 3.3 wt% C and 54.8 wt% ± 6.3 wt% O, Table 1, Figure 2; these values are averages over 45 data points measured on five different surface sites for each of the nine samples. The average root mean square (RMS) surface roughness measured was 20.12 nm (± 16 nm), Table 2; which is very smooth. For such smooth surfaces no significant influence on CO\(_2\)-wettability was observed.\(^{[17]}\) Furthermore, contact angles on these pure calcite samples were (advancing 0° and
receding 0°) at ambient conditions, thus pure calcite was completely water-wet at ambient conditions. However, higher contact angles (advancing 48° and receding 40°) and (advancing 68° and receding 62°) were measured at reservoirs conditions on these pure calcite samples (323 K, 10 MPa and 25 MPa), consistent with literature data.[61,62]

**Aged calcite**

Aging had no significant influence on surface roughness (20.58 nm ± 16 nm), Table 2. However, the atomic surface concentrations changed due to chemisorption of the carboxylic acids on the calcite surface, consistent with Zullig and Morse (1988).[42] The new average surface atomic content of the treated samples was 22.7 wt% ± 5.1 wt% Ca, 22.9 wt% ± 3.6 wt% C and 54.4 wt% ± 5 wt% O, Table 1, Figure 2. Thus, a significant overall average increase in surface carbon concentration (+2.3 wt% C) was observed due to surface stearate adsorption (Table 1).

Furthermore, aging of the calcite surfaces caused a significant change in contact angles and thus CO₂-wettability, this is discussed in detail below.

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**Table 1.** Surface composition of pure and aged calcite and change due to ageing.

<table>
<thead>
<tr>
<th>Stearic Acid Concentration (Molarity)</th>
<th>Pure calcite</th>
<th>After ageing</th>
<th>Change due to ageing</th>
<th>Estimated surface coverage[14]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt% Ca</td>
<td>wt% C</td>
<td>wt% O</td>
<td>wt% Ca</td>
</tr>
<tr>
<td>10⁻²</td>
<td>24.9</td>
<td>18.8</td>
<td>56.3</td>
<td>23.2</td>
</tr>
<tr>
<td>10⁻³</td>
<td>25.8</td>
<td>18.4</td>
<td>55.9</td>
<td>23.2</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>25.1</td>
<td>21.3</td>
<td>53.6</td>
<td>24.8</td>
</tr>
<tr>
<td>10⁻⁵</td>
<td>22.0</td>
<td>20.0</td>
<td>58.0</td>
<td>21.6</td>
</tr>
<tr>
<td>10⁻⁶</td>
<td>28.0</td>
<td>24.9</td>
<td>47.2</td>
<td>22.1</td>
</tr>
<tr>
<td>10⁻⁷</td>
<td>24.0</td>
<td>20.4</td>
<td>55.7</td>
<td>22.5</td>
</tr>
<tr>
<td>10⁻⁸</td>
<td>25.6</td>
<td>20.0</td>
<td>54.4</td>
<td>20.9</td>
</tr>
<tr>
<td>10⁻⁹</td>
<td>28.3</td>
<td>19.6</td>
<td>52.1</td>
<td>28.2</td>
</tr>
<tr>
<td>10⁻¹⁰</td>
<td>18.6</td>
<td>21.5</td>
<td>59.8</td>
<td>18.0</td>
</tr>
<tr>
<td>0</td>
<td>20.9</td>
<td>20.1</td>
<td>59.0</td>
<td>20.9</td>
</tr>
</tbody>
</table>
Table 2. Contact angle measurements and Surface Roughness (AFM*) at different stearic acid concentrations

<table>
<thead>
<tr>
<th>Stearic acid concentration (Molarity)</th>
<th>Initial RMS* surface roughness (nm), pure calcite</th>
<th>Final RMS* surface roughness (nm), treated calcite</th>
<th>CO₂/Calcite/brine contact angle (10 MPa and 323 K)</th>
<th>CO₂/Calcite/brine contact angle (25 MPa and 323 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>θa</td>
<td>θr</td>
<td>θa</td>
<td>θr</td>
</tr>
<tr>
<td>10⁻²</td>
<td>4.4</td>
<td>4.8</td>
<td>126.0 (n=3)</td>
<td>98.6 (n=3)</td>
</tr>
<tr>
<td>10⁻³</td>
<td>13.4</td>
<td>13.9</td>
<td>108.2 (n=3)</td>
<td>91.8 (n=3)</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>25.3</td>
<td>26.2</td>
<td>100.9 (n=3)</td>
<td>86.5 (n=3)</td>
</tr>
<tr>
<td>10⁻³</td>
<td>37.1</td>
<td>37.6</td>
<td>65.7 (n=3)</td>
<td>49.5 (n=3)</td>
</tr>
<tr>
<td>10⁻⁵</td>
<td>25.9</td>
<td>26.4</td>
<td>53.5 (n=3)</td>
<td>37.2 (n=3)</td>
</tr>
<tr>
<td>10⁻⁶</td>
<td>27.2</td>
<td>27.5</td>
<td>51.4 (n=3)</td>
<td>37.2 (n=3)</td>
</tr>
<tr>
<td>10⁻⁷</td>
<td>18.6</td>
<td>19.2</td>
<td>49.7 (n=3)</td>
<td>37.2 (n=3)</td>
</tr>
<tr>
<td>10⁻⁸</td>
<td>7.2</td>
<td>7.5</td>
<td>45.6 (n=3)</td>
<td>37.2 (n=3)</td>
</tr>
<tr>
<td>10⁻⁹</td>
<td>21.6</td>
<td>22.1</td>
<td>43.1 (n=3)</td>
<td>37.2 (n=3)</td>
</tr>
</tbody>
</table>

*RMS – Route Mean Square

*AFM - Atomic Force Microscopy

n - The number of repeated experiments at the conditions indicated

2.2.3 Contact angle measurements

CO₂-wettability was determined by contact angle measurements at reservoir conditions (i.e. 323 K, at 10 MPa and 25 MPa) using a tilted plate goniometric setup.[60,63] The experimental setup consisted of a high pressure-high temperature cell that can operate at reservoir conditions. The substrate was placed in a tilted angle of (17º) inside the cell. Two separate high precision syringe pumps (Teledyne D-500, pressure accuracy of 0.1%) adjusted the CO₂ pressure, or injected the brine. The detailed setup has been described earlier.[61,64]

Experimentally, the sample was placed inside the pressure cell on the tilted plate and the cell was heated to the desired temperature (323 K). Subsequently the CO₂ pressure was raised to prescribed values (10 MPa and 25 MPa), and a droplet of degassed brine with an average volume of 6 µL (± 1 µL) was dispensed onto the calcite surface through a needle. The advancing (θa) and receding (θr) water contact angles were then measured at the leading and trailing edge of the droplet just before the drop started to move.[63] A high-resolution video camera (Basler scA 640–70 fm, pixel size = 7.4 µm; frame rate = 71 fps; Fujinon CCTV lens:
HF35HA-1B; 1:1.6/35 mm) captured movies of these processes, and \( \theta_a \) and \( \theta_r \) were measured on images extracted from the movie files. The standard deviation of the measurements was \( \pm 3^\circ \) based on replicated measurements.

3. **Results and Discussion**

CO\(_2\)-wettability of a storage formation is a key parameter which strongly influences CO\(_2\) movement and distribution throughout the formation,

\(^{[9,34]}\) rate of injectivity,\(^{[4,5]}\) storage capacity and containment security,\(^{[35,64,65]}\) It is thus vital to understand CO\(_2\)-wettability in detail.

In this context, the water receding contact angle (i.e. CO\(_2\) displacing water) is related to structural trapping (below an impermeable caprock).\(^{[13]}\) The advancing contact angle (water displacing CO\(_2\)) determines the capillary trapping capacity\(^{[66]}\) and thus the amount of residually trapped CO\(_2\).\(^{[6-8]}\) It has also been shown in previous studies that dissolution trapping is significantly affected by the wettability, and it is thus necessary to know the wettability for accurate reservoir simulations and storage capacity predictions.\(^{[9,34]}\)

We thus conducted contact angle measurements with different mineral surface chemistry scenarios at various thermo-physical conditions. The minute concentrations of stearic acid exposed to the substrates (which represents the small amounts of organic acid molecules in deep saline aquifer storage formations) had a highly significant influence on the water-wetness of the rock.

The results show that calcite rapidly loses its water-wetness with increasing stearic acid surface coverage (Figure 1), i.e. higher organic acid concentration led to significantly higher CO\(_2\)-wettability. For instance, at 323 K and 25 MPa, a carbonate storage formation having \( 10^{-10} \) M stearic acid is weakly water-wet (\( \theta_r = 64.3^\circ \)), while \( \theta_r \) reached 90\(^\circ \) at \( 10^{-4} \) M stearic acid exposure concentration (note that capillary leakage is possible at \( \theta_r > 90^\circ \)).\(^{[4,5,56,67]}\)
The optimal capillary trapping limit, which we define here as the point where primary drainage is unaffected by wettability is at $\theta_a = 50^\circ$. $\theta_a$ is even more affected by the carboxylic acids concentration; even at a relatively low pressure of 10 MPa (note that increasing pressure increases $\theta$)\cite{4,17} and 323 K, $\theta_a$ reaches 50° at $10^{-10}$ M carboxylic acids concentration (note that this is a very minute concentration, much higher carboxylic acids concentration are measured in deep saline aquifers\cite{22-27} and for 25 MPa this organic threshold is even below $10^{-10}$ M (Figure 1).

Figure 1: CO$_2$/calcite/brine (water) contact angles measured as a function of stearic acid concentration at 323 K and 10 MPa and 25 MPa; $C_{\text{organic}}$ is the stearic acid concentration (molarity). Dotted green line represents the structural trapping limit, while the blue dotted line represents the optimal capillary trapping limit. The zone above the dotted green line indicates the reduced CO$_2$ zone.
Figure 2: SEM images before and after treatment with $10^{-2}$ M organic acid, (a) before treatment, (b) after treatment

The SEM images of the calcite surfaces were acquired before and after treatment with stearic acid; two examples are shown in Figure 2. It is clear that the texture of the image without stearic acid (Figure 2a) is quite transparent whereas a clear spread of organic acid on the calcite surface can be observed after surface treatment with $10^{-2}$ M stearic acid (Figure 2b). This stearic acid coverage of the calcite surface is responsible for the wettability change from strongly water-wet to weakly CO$_2$-wet

Physically, the shape of the droplet spreading on the calcite surface observed during the contact angle measurement also indicates the wetting behaviour (Figure 3). It is clear that the brine droplet almost completely spread on the pure calcite surface at 10 MPa (Figure 3a), implying water-wet conditions. On the contrary, the brine droplet only showed a minimal spread on the surface treated with $10^{-2}$ M stearic acid (measured at 25 MPa; Figure 3d) resulting in a higher water contact angle.
Figure 3: Contact angle images of different calcite surfaces, (a) pure calcite at 10 MPa, (b) pure calcite at 25 MPa, (c) aged calcite with $10^{-2}$ M organic acid at 10 MPa, (d) aged calcite with $10^{-2}$ M organic acid at 25 MPa

The implications of the results can be investigated via a capillary force – buoyancy force balance\textsuperscript{[69]} as follows:

$$h = \frac{2\gamma \cos \theta_r}{\Delta \rho g R}$$

\textit{Eq. 1}

where ‘\(h\)’ is the height of the CO\(_2\) column immobilized beneath the seal layer, ‘\(\gamma\)’ is CO\(_2\)-brine interfacial tension, ‘\(\theta_r\)’ is the receding contact angle, ‘\(\Delta \rho\)’ is the CO\(_2\)-brine density difference, ‘\(g\)’ is the gravitational acceleration, and ‘\(R\)’ is the caprock’s average pore throat radius.

Thus, for a limestone storage formation at 10 MPa and 323 K, three main cases can be distinguished: a) pure calcite, b) storage rock exposed to $10^{-6}$ M stearic acid, and c) storage rock exposed to $10^{-2}$ M stearic acid.
The corresponding ‘\(\theta_r\)’ values under these conditions are 45°, 55° and 100° (Figure 1). The ‘\(\gamma\)’ and ‘\(\Delta \rho\)’ values at 10 MPa and 323 K are 40 mN/m from\(^{[69]}\) and 683 kg/m\(^3\) interpolated from\(^{[70]}\) respectively; while a typical caprock pore radius is 0.01 \(\mu\)m from\(^{[71]}\). \(\text{CO}_2\) column heights ‘\(h\)’ calculated using Eq. (1) are thus 916 m for the case of pure calcite, 685 m for the case of \(10^{-6}\) M stearic acid exposure, and -207 m for the calcite surface exposed to \(10^{-2}\) M stearic acid (Figure 4). It is therefore clear that with increasing stearic acid concentration, the structural storage capacity reduces significantly. Moreover, the column height reached a negative value (-207 m) at \(10^{-2}\) M stearic acid concentration, indicating \(\text{CO}_2\) leakage due to wettability reversal (Figure 4).

**Figure 4.** \(\text{CO}_2\) column heights estimated as a function of stearic acid concentration at 10 MPa and 323 K. For \(10^{-2}\) M stearic acid concentration, the height is negative which implies \(\text{CO}_2\) leakage (column in negative y-axis). The graphic at the intersect of each column illustrates a hypothetical storage scenario where the black semi-circular region represents the storage rock, orange bubbles inside represent \(\text{CO}_2\), and the red line at the top represents the seal layer. The left column (no organic present) shows \(\text{CO}_2\) bubbles occupying a larger height as compared to the second column, which indicates a decrease in structural trapping due to presence of organic acid, whereas the column on the right shows potential \(\text{CO}_2\) leakage due to wetting alteration to weakly \(\text{CO}_2\)-wet at higher organic acid concentrations.
Furthermore, the wettability alteration found in this work can be explained by the interplay of the interfacial tensions (‘γ’) which are related by the Young’s equation as follows:

\[
\cos \theta = \frac{\gamma_{sv} - \gamma_{st}}{\gamma_{vl}} \quad \text{Eq. 2)
\]

In Eq. (2), ‘γ_{sv}’ is the calcite-CO\(_2\) interfacial tension, ‘γ_{st}’ is the calcite-brine interfacial tension, and ‘γ_{vl}’ is the CO\(_2\)-brine interfacial tension. At a given pressure and temperature, the numerator in equation (2) decreases with increasing stearic acid concentration as ‘γ_{sv}’ decreases with increasing stearic acid coverage\(^{[14,69]}\). Thus, as ‘γ_{st}’ is a constant at constant pressure and temperature, the adsorption of stearic acid on the calcite surface results in a higher water contact angle and de-wetting of the surface.

It is thus clear that a precise knowledge of the organic acid concentrations in a storage reservoir is essential for assessing the conditions for long-term geological storage. A pertinent limitation, however, is that current data applies to carbonate/limestone formations, and a broader consideration of various organic acid molecules and minerals may provide better insights.

Moreover, We note that it has been previously shown for quartz surfaces that divalent cations result in further contact angle increase due to the stronger surface screening effect of the divalent ions (in comparison with the corresponding monovalent ions), thus reducing the surface potential and surface hydrophilicity – which results in higher contact angles\(^{[4,17]}\).

4. Conclusions

Deep saline aquifers and depleted hydrocarbon reservoirs are the most important sinks for CO\(_2\) geological storage\(^{[1,73]}\). However, it has been shown that the CO\(_2\)-wettability of the storage and seal rock dramatically influences the injectivity, storage capacity, containment security\(^{[14,5,9,34,35,64,65]}\) and thus project economics and technical feasibility.
Realistic subsurface conditions have, however, not been tested, and the focus was on clean mineral substrates, which, however, do not exist in the subsurface (as in the subsurface anoxic or reducing conditions prevail, while clean mineral surfaces can only exist in strongly oxidising conditions).\cite{18,20}

We therefore measured the CO$_2$-wettability on carbonate mineral surfaces which mimic these subsurface storage conditions of carbonate reservoirs more realistically. This representativeness was achieved by exposure to a highly diluted carboxylic acids ($10^{-2} - 10^{-10}$ M), and measurements were conducted at realistic storage conditions (10 MPa and 25 MPa and 323 K). Clearly, even minute exposure to traces of such organic acid molecules significantly increased the water contact angle (θ), and thus CO$_2$-wettability. This effect drastically increased with higher organic acid concentration and pressure.

We thus conclude that CO$_2$ geological storage capacities and containment security can be significantly lower than previously thought. Reservoir-scale models thus need to take these effects into account so that accurate storage predictions are obtained thus de-risking carbon geological storage (CGS) projects.
Conflicts of Interest

There are no conflicts to declare.

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