Review of the Effects of CO₂ on Very-Fine-Grained Sedimentary Rock/Shale – Part III: Shale Response to CO₂

2 November 2017
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Cover Illustration: Stylized figure depicting the flow of supercritical carbon dioxide through a fine-grained rock mass in contrast with a photomicrograph of clay minerals that potentially can swell and impede flow (Figures modified from http://www.rigzone.com/news/oil_gas/a/124801/Musings_Will_Barnett_Shale_Study_End_Debate_Over_Gas_Outlook and from Evelyne Delbos, at http://www.minersoc.org/photo.php?id=143)


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Review of the Effects of CO₂ on Very-Fine-Grained Sedimentary Rock/Shale -
Part III: Shale Response to CO₂

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<td><strong>Acronyms/Abbreviations</strong></td>
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</tr>
<tr>
<td>0W, 1W, 2W, 3W</td>
<td>Hydration states of clay structure</td>
</tr>
<tr>
<td>ASTM</td>
<td>ASTM International</td>
</tr>
<tr>
<td>(aq)</td>
<td>Aqueous</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller isotherm type</td>
</tr>
<tr>
<td>CN</td>
<td>Changning Region, China</td>
</tr>
<tr>
<td>CT</td>
<td>Computed tomography</td>
</tr>
<tr>
<td>d001</td>
<td>Miller Index, 001 = basal spacing</td>
</tr>
<tr>
<td>FL</td>
<td>Fuling Region, China</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>HADES</td>
<td>High Activity Disposal Experimental Site</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
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<td>NETL</td>
<td>National Energy Technology Laboratory</td>
</tr>
<tr>
<td>NLDFT</td>
<td>Non-localized density functional theory</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>sc</td>
<td>Supercritical</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic content</td>
</tr>
<tr>
<td>UCS</td>
<td>Uniaxial compression strength</td>
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<tr>
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<td>C₂H₃NaO₂</td>
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## Acronyms, Abbreviations, Symbols (cont.)

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<tr>
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<td>gram</td>
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<tr>
<td>g/g</td>
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<td>gram per Liter</td>
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<td>kg/t</td>
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<td>liter</td>
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<td>L/day</td>
<td>liter per day</td>
</tr>
<tr>
<td>M</td>
<td>molarity or molar concentration; mol/L</td>
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<tr>
<td>m</td>
<td>meter</td>
</tr>
<tr>
<td>m³/s</td>
<td>cubic meter per second</td>
</tr>
<tr>
<td>mD</td>
<td>millidarcy ($10^{-3}$ D); ($= 9.86923266716 \times 10^{-16}$ m²)</td>
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<tr>
<td>mg</td>
<td>milligram ($10^{-3}$ g)</td>
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<tr>
<td>mg/L</td>
<td>milligram per liter</td>
</tr>
<tr>
<td>mg/dm³</td>
<td>milligram per cubic decimeter (dm³ = 10⁻³ m³)</td>
</tr>
<tr>
<td>mL</td>
<td>milliliter ($10^{-3}$ L)</td>
</tr>
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<td>minute</td>
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<tr>
<td>mL/min</td>
<td>milliliter per minute</td>
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<tr>
<td>mm</td>
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<td>megaohm-cm ($10^{6}$ ohm - cm)</td>
</tr>
<tr>
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<td>newton per minute</td>
</tr>
<tr>
<td>N</td>
<td>newton (kg m per s²)</td>
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<td>µJ</td>
<td>microjoule ($10^{-6}$ J); ($J = kg m^2 per s^2$)</td>
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<td>µL</td>
<td>microliter ($10^{-6}$ L); ($= 1$ mm³)</td>
</tr>
<tr>
<td>µm</td>
<td>micron or micrometer ($10^{-6}$ m)</td>
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<tr>
<td>µM</td>
<td>micromolar ($10^{-6}$ mol per L)</td>
</tr>
<tr>
<td>ηD</td>
<td>nanodarcy ($10^{-9}$ D); ($= 9.86923266716 \times 10^{-22}$ m²)</td>
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<tr>
<td>ηm</td>
<td>nanometer (10^{-9} \text{ m})</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>psi, psia</td>
<td>pound per square inch; absolute</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
</tr>
<tr>
<td>scf</td>
<td>standard cubic foot of gas [measured at 70 °F (21 °C) at 14.696 psia (101.35 kilopascals)]</td>
</tr>
<tr>
<td>ton</td>
<td>short ton (2,000 pounds)</td>
</tr>
<tr>
<td>t, tonne</td>
<td>metric ton (1,000 kg)</td>
</tr>
<tr>
<td>vol%</td>
<td>percent by volume</td>
</tr>
<tr>
<td>wgt%</td>
<td>percent by weight</td>
</tr>
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</table>
Acknowledgments

This work was completed as part of National Energy Technology Laboratory (NETL) research for the U.S. Department of Energy’s (DOE) Carbon Storage Program. The author wishes to acknowledge Cindy Powell and Traci Rodosta (NETL Research & Innovation Center) as well as Angela Goodman (NETL Technical Portfolio Manager Carbon Storage) for guidance, direction, and support.

In addition, the author wishes to thank Dustin Crandall (Task Technical Coordinator, Geological and Environmental Systems, NETL Research & Innovation Center) for his technical review, direction, and support.
EXECUTIVE SUMMARY

Carbon dioxide (CO₂) (which occurs naturally underground) has recently seen increased use in various industrial subsurface applications. In response, a comprehensive review was initiated to investigate the potential effects of CO₂ exposure on a very-fine-grained sedimentary rock/mudstones, based on existing experimental data. An emphasis of this study was to characterize the potential of shale (a mudstone) to swell when exposed to CO₂, and how to identify the potential for swell when CO₂ is used at a specific site.

This report is the third in a sequence of reports from this study¹ and examines the observed effects of CO₂ on shale performance, surveying the current literature on experimental results to identify important trends. Experimental results for CO₂ sorption, CO₂-induced swell, chemical reactions and permeability tests with CO₂ were reviewed and are discussed in detail in the attached appendices. The main text of this report describes the general findings on each of these topics and makes recommendations for future testing. In addition, a short discussion on the aspects of subsurface CO₂ flow is also included to provide some context for CO₂ testing and to recognize the importance of coupling in simulating CO₂ flow.

Major conclusions of this review are:

1. The mineralogy of a mudstone (especially a shale) is fundamental in understanding the potential for swell and chemical reactivity. The aspects of clay content, the type and amount of clay minerals, and the organic content of the rock together with the shale fabric, all play a direct role in assessing the suitability of a rock unit for engineering applications.

2. CO₂ and water interact with the mudstone fabric in determining the amount of sorption and in the swell of the rock. Therefore, the initial water content of mudstone has a major influence on response.

3. Chemical interactions of mudstone with CO₂ and brine occurs both over the short-term (days) and over the long-term (years). However, experiments require several days of CO₂ exposure to exhibit the effects of alteration in short-term testing. Data on long-term testing with CO₂ response is scarce and insufficient to fully define the long-term impact of interactions on activities such as geosequestration.

4. CO₂ can have a significant effect on mechanical properties of mudstone (including the degree of anisotropy), and this effect is orientation-dependent.

5. Swelling of a few mudstones with CO₂ has been observed in the laboratory. The observed extent of swelling, however, appears to be minor in lab-scale tests with deformations only on the order of a few percent. In some cases, no swell is observed with shales. This is in contrast to microscopic observations (with tests measuring clay mineral-layer spacings), which indicate swelling strains as large as 60%.

¹ For prior progress reports, see Lindner (2016a, 2016b).
6. Flow of CO$_2$ alone (i.e., anhydrous CO$_2$) through mudstones can dehydrate the rock matrix, inducing shrinkage and fracturing of the rock under specific conditions.

7. The initial chemical reaction of shale to CO$_2$ is dominated by carbonic acid. The amount of water present enhances the reactivity of the CO$_2$ with the rock. Exposure of mudstones to CO$_2$ will induce reactions with various component minerals, especially dolomite and calcite.

8. The sorption of CO$_2$ on mudstones varies with gas pressure and does not follow a typical Langmuir or BET isotherm. The CO$_2$ excess sorption isotherm of a mudstone initially increases with increasing gas pressures to about 5 to 7 MPa, but later, the isotherm decreases significantly with increasing pressure (above 10 MPa), trending sometimes to zero.

9. Varying processes occurring in fractures with CO$_2$ flow can enhance or degrade flow through the rock mass. The aperture of the flow channels can be increased substantially due to dissolution, but the flow can also be obstructed by precipitation along secondary channels. In addition, these processes can alter the primary flow path or the overall flow network with time.

10. It is strongly recommended that additional test development and research be conducted on this topic. Given the lack of data on the various subtopics, the difficulties and shortcomings in current test procedures, and the requisite for a better understanding the interaction of CO$_2$ and mudstones for engineering applications, the need is paramount.
1. INTRODUCTION

1.1 SCOPE

This report is the third in a series of reports that reviews the current state of knowledge on the response of very-fine-grained sedimentary rocks to the flow of carbon dioxide (CO₂) and brine. Of particular interest, the multi-part review focuses on the potential for rock expansion and contraction (typically stated as rock swell) induced by CO₂ in shales to affect fracture aperture, fluid flow, and rock properties important for geologic carbon storage and enhanced oil/gas recovery.

The present volume examines the experimental data on the response of clay minerals and shale² to CO₂ exposure, summarizing the effects and trends over a range of conditions. The review of this experimental work is subdivided along several major lines of study involving sorption, swell, chemical reactions, and permeability. A brief examination of aspects of CO₂ flow in the subsurface is also included to provide a context for future experimentation.

In conducting this review, selected references were summarized in depth, and these summaries are included in the appendices of this report. The main text summarizes the principal results of these references to identify general aspects and critical factors in CO₂ effects on very-fine-grained mudstones to construct generalizations on shale behavior and guide additional research and modeling.

1.2 PROBLEM STATEMENT

CO₂ exists naturally in the subsurface, together with various fluids (brine, petroleum hydrocarbons) and gases³ such as carbon monoxide (CO), methane (CH₄), hydrogen sulfide (H₂S), and noble gases. In recent years, CO₂ has been injected in the subsurface to enhance hydrocarbon recovery production and for geothermal energy studies. Geologic storage of CO₂ is also being studied to address issues of climate warming. As these efforts are often conducted at substantial depths in saline environments, the resulting subsurface fluids are a combination of CO₂ in a supercritical phase (scCO₂) and a multi-component brine. Given that scCO₂ is less dense than the native brine, buoyancy drives CO₂ upwards after injection, passing through the more permeable injection horizon (say a sandstone or limestone unit) until encountering a less-permeable horizon, often a mudstone unit, and frequently identified as a “caprock” layer.

The CO₂ flow through these layers can have significant consequences in application. For CO₂ sequestration, the caprock limits the upward CO₂ flow into the biosphere. Potential flow or leakage through a caprock is a dynamic process, as the scCO₂-brine is expected to interact with the rock layer, which in turn will influence the transmissibility of the material system. Some of these physiochemical reactions may increase the transmissibility, while other reactions may

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² The definitions of shale and mudstone are provided in Part I of this report series (Lindner, 2016a).
³ Many of these gases are liquids at depth.
substantially reduce the flow. These reactions also pertain to applications where the formation is used to store scCO₂.

The results of this overall study on shale-CO₂ interactions at NETL are presented in a set of reports. In each report, a set of relevant topics are critically examined, identifying limitations and making recommendations to address issues in current technology.

This is the final report in the series, focusing on the effect of CO₂ directly on various aspects of response that can affect swell of mudstones. Aspects such as CO₂ sorption, swell, chemical reactions, and the effects of CO₂ on mechanical response and fracture flow are examined to draw generalizations from current observations. The results are used to identify general trends in response, as well as areas where additional data is needed and provide a basis for recommendations for ongoing research.
2. **OBSERVED EFFECTS OF CO$_2$ ON CLAY AND MUDSTONE**

2.1 **THE RANGE OF EXPERIMENTAL EVIDENCE**

In examining available literature on possible types of CO$_2$-brine-shale interactions, the experimental evidence reviewed for this report focused on five specific categories:

1. CO$_2$ sorption by clay minerals and by shales and other mudstones.
2. Swell of clay minerals and mudstones induced by CO$_2$.
3. Chemical reactions of CO$_2$ and brine with shale.
4. Mechanical property (e.g., modulus, strength) changes due to CO$_2$ exposure.
5. Effects of CO$_2$ flow on the permeability of intact and fractured rock.

Although these topics are discussed independently, the various processes of CO$_2$ flow (i.e., thermal, mechanical, hydrological, chemical, biological) are coupled together in the overall system. One example of this coupling is the products of geochemical reactions that affect the mechanical characteristics of fracture apertures, altering the flow field and flow velocity, with the resulting changes influencing the speed and type of chemical reactions.

The interrelationship of these processes is not always well represented in the laboratory. Conceptually, the sorption of CO$_2$ by shale should be correlated to the swell response of shales. However, the sorption of low permeability materials (such as shale) is typically measured on crushed, uncompacted samples without volume control or measurement. As a result, the interrelationship between sorption and the expansion of shale has not been well demonstrated experimentally and the topics of sorption and swell are discussed separately in this report.

2.2 **CO$_2$ SORPTION**

2.2.1 **General**

Clay minerals (such as montmorillonite, kaolinite, and illite) together with mudstones sorb CO$_2$ as well as other gases, as frequently observed in the laboratory and during field activities. Sorption data with these geomaterials are reported in an extensive body of literature, and detailed summaries of some of this experimental work are provided in Appendix A. The discussion in this section is subdivided between testing on clay minerals (to provide a general basis for understanding of CO$_2$ sorption response) and tests performed on mudstone/shale samples.

Implicit in this discussion is the assumption that CO$_2$ sorption will induce a volumetric change in the clay minerals and in rock containing clay minerals. As for hydration swell of clays (Lindner, 2016b), the amount of volumetric change due to sorption can be expected to be dependent on the initial condition of the material (especially the water content), on external factors, and on the fabric of the material itself.

2.2.2 **CO$_2$ Sorption by Clay Minerals**

The sorption and desorption of CO$_2$ by clays was initially studied at low temperatures by authors such as Thomas and Bohor (1968) and Aylmore et al. (1970). As discussed by Giesting et al.
(2012a), Schaef et al. (2012), and Romanov et al. (2013), these studies disputed whether CO₂ could enter the interlayers of montmorillonite, or whether it is sorbed only to external crystallite surfaces. Intercalation was more conclusively shown by Fripiat et al. (1974) at -70 °C, but questions remain and results are expected to vary with clay mineral structure.

Recently, several experiments have been conducted on CO₂ sorption with clays at conditions more relevant to subsurface CO₂ storage and use. CO₂ sorption testing with clay minerals has been performed over a temperature range of 20 °C to 130 °C, and at pressures up to 20 MPa. These studies (Appendix A.1) demonstrate that CO₂ sorption occurs at these conditions over the range of clay minerals including montmorillonite, illite, and kaolinite.

While CO₂ sorption by clays is relatively small, it is significant and can be readily measured. The amount of CO₂ sorption varies with clay mineral type, with montmorillonite sorbing more than other clay minerals (Busch et al., 2008). Ca-montmorillonite, in particular, absorbs more than Na-montmorillonite by a substantial margin (Romanov, 2013; Schaef et al., 2015) and the Ca-sorption isotherm is larger by a factor of two or more (Busch et al., 2008; Jeon et al., 2014). In turn, the sorption of Na-montmorillonite is significantly greater than for other clay minerals (Busch et al., 2008). Similarly, illite sorbs significantly more CO₂ than kaolinite (Busch et al., 2008; Heller and Zoback, 2014). Finally, kaolinite absorbs more than chlorite, as noted by Busch et al. (2008); the amount sorbed by chlorite can be considered negligible (Busch et al., 2016).

Schematically, the amount of CO₂ sorption occurs in the following order:

\[
\text{Ca-montmorillonite} \gg \text{Na-montmorillonite} > \text{illite} > \text{kaolinite} > \text{chlorite}
\]

Based on the literature reviewed and presented in Appendix A, some typical sorption values are shown in Table 1.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Typical Peak Excess Sorption Values (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-montmorillonite</td>
<td>1.2 to 1.4</td>
</tr>
<tr>
<td>Na-montmorillonite</td>
<td>0.4 to 0.6</td>
</tr>
<tr>
<td>Illite</td>
<td>0.2 to 0.4</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0.1 to 0.2</td>
</tr>
</tbody>
</table>

Notes:

\[a\] Peak sorption at stresses less than 6 MPa.

\[4\] Results studying the sorption of CH₄ by clays indicate a somewhat different order in clay types, i.e.: kaolinite > chlorite > illite, as noted by Ji et al. (2012).
These excess sorption values of clays and isotherms for CO$_2$ are strongly gas pressure dependent. Below pressures of approximately 5 MPa, the CO$_2$ isotherm increases with increasing pressure, but at a decreasing rate and appears to be almost asymptotic at the peak. This shape is often described as a Langmuir isotherm (or Type I curve, shown in Figure 1) per the International Union of Pure and Applied Chemistry (IUPAC) classification system as discussed by Clarkson and Haghshenas (2013).\textsuperscript{5}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Langmuir_BET_isotherms.png}
\caption{Typical Langmuir and BET isotherms.}
\end{figure}

In some cases, at roughly 7 MPa, the rate of sorption by clays can change significantly with the isotherm increasing to a distinct peak (e.g., Schaef et al., 2014a). This is similar to a typical BET\textsuperscript{6} isotherm or IUPAC Type II curve (Clarkson and Haghshenas, 2013).

However, at higher pressures, many CO$_2$ isotherms of clay minerals exhibit a more complex response than described by these theoretically-based curves. At pressures greater than roughly 5 to 10 MPa, the excess sorption isotherm rate for clay can dramatically decrease, and the sorption isotherm reduces to a value less than 50% of the peak value (Busch et al., 2008) or tends to zero (Jeon et al., 2014). This decrease is typically rapid with increasing pressure (completing the decline within 2 to 3 MPa from the peak) and attaining a new, but lower limit at pressures of less than about 12 MPa. Note that this transition behavior bounds the pressure limit for supercritical CO$_2$ at 7.38 MPa (NIST, 2016a), so the rapid decrease may reflect (to some degree) the CO$_2$ phase change from a gas to a supercritical fluid.

CO$_2$ sorption on clays is also dependent on temperature to a lesser degree. Testing of Na-montmorillonite over a range of temperature 30 °C to 127 °C indicated that CO$_2$ sorption is

\textsuperscript{5} Excess sorption of CH$_4$ and N$_2$ show this typical shape over the entire pressure range.

\textsuperscript{6} BET = Brunauer-Emmett-Teller.
inversely temperature dependent, with sorption decreasing 40% with increasing temperature over
this range (Pribylov et al., 2010). Other testing indicated about 15% decrease in sorption on
montmorillonite from 45 °C to 55 °C (Jeon et al., 2014) and a roughly a 45% decrease over a
temperature range of 60 to 120 °C (Breig, 2010). This sorption change with montmorillonite,
however, is not completely uniform with temperature, as the rate of decrease in sorption changes
with increasing temperature (with less change in sorption for the same change in temperature).
The temperature dependence was also not as apparent in other clay minerals, as the CO2 sorption
on illite and kaolinite appears essentially temperature-independent with little change in sorption
values seen from 45 °C to 55 °C (Jeon et al., 2014).

In addition, the CO2 sorption process has been observed to be path dependent, as the CO2
isotherm can show significant hysteresis in sorption/desorption, and can show a large residual
sorption values when pressure is reduced (Romanov, 2013; Jeon et al., 2014). In some cases, the
desorption value is significantly larger than the original value evidenced during sorption (Jeon
et al., 2014). Re-testing the same sample can also show a significant reduction in sorption, as
shown by Busch et al. (2008); this decrease, however, may be due to a change in the fabric
induced by reloading the sample by the authors.

Of importance to field applications, CO2 sorption is also dependent on the current water content
of the clay minerals, apparently exhibiting an inverse function of sorption to water content. As
shown by Busch et al. (2008), drying the clay minerals prior to testing causes a significant
increase in the magnitude of the CO2 sorption with various clay minerals. For
Ca-montmorillonite, an increase of 30% in peak response was observed after drying the sample
from an as-received water content of 9.7%. Also, as described by Kumar (2016), pressure
soaking an illite sample reduced the peak sorption from about 3.5 mmol/g of a dry sample to less
than 0.1 mmol/g on the wet illite. Unfortunately, sorption experiments are often performed on
treated and dried samples, and therefore, the magnitude of this behavior cannot currently be
assessed from the literature. This behavior indicates that laboratory values (in a dried state)
provide maximum “potential” sorption values in contrast to the “actual” or in situ sorption that is
evident with clay mineral formations at some natural moisture state. It also suggests that CO2
does not replace water (H2O) in the clay mineral structure, but rather interacts with H2O to
achieve some form of equilibrium.

In general, the sorption of CO2 by clay minerals is larger than that for other gases such as CH4,
CO, and nitrogen (N2) (Venaruzzo et al., 2002; Heller and Zoback, 2014). It is also greater than
helium (He), which shows no measurable sorption on clay and is therefore often used as a
control in experimental studies. Conversely, CO2 sorption is less than that of other gases used in
the petroleum field such as sulfur dioxide (SO2) (Venaruzzo et al., 2002). As suggested by
Breig (2010), the sorption by clay minerals can correlate with the boiling point of the sorbing
fluid. Specifically, the boiling point serves as a reference property indicative of the volatility of
the gas phase as illustrated in Figure 2.

\[7 \text{ In this case, the clay mineral is not specified.} \]
2.2.3 Sorption of Mudstones/Shales

2.2.3.1 Pressure Dependence

CO₂ sorption testing on shales or mudstones\(^8\) has been performed by various authors at conditions representative for sequestration (see Appendix A.1.2). These test results show that the CO₂ adsorptive capacity of mudstones/shales is less than other rock types, such as coal (e.g., Chareonsuppanimit et al., 2012). Like clay mineral testing, experiments have also shown that CO₂ can have a significantly higher adsorptive capacity in mudstones than other gases such as CH₄ or N₂, especially at lower pressures (e.g., Heller and Zoback, 2013).

As for clay minerals, CO₂ has been observed in the laboratory to be sorbed by mudstones as an atypical function\(^9\) of pressure over a temperature range of 5 to 85 °C. The CO₂ isotherm trend can be divided for discussion into three distinct zones/phases versus pressure, along the lines indicated Busch et al. (2008).

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\(^8\) With some authors, the use of the term shale is generic, and simply refers to a very-fine-grained sedimentary rock, which otherwise would be better termed a mudstone (see Lindner, 2016a).

\(^9\) This curve is not shown in the IUPAC system. However, it approximates a Type 2 curve in for the classification system proposed by Donohue and Aranovich (1999) for sorption near the critical point.
These three zones or phases are illustrated in Figure 3:

1. Phase #1 - Increasing Phase: at lower pressures (less than 5 to 7 MPa), CO2 sorption increases with increasing pressure, presenting an asymptotic trend. This type response is typical of other gases (e.g., CH4 and N2).

2. Phase #2 - Distinct Peak Phase: at intermediate pressures, sorption isotherms can show an abrupt, steep increase, rising to a sharp peak in response, typically with a maximum at a pressure of about 10 MPa. However, this peak response is not always present in experimental results, and the isotherm can trend from Phase #1 directly into Phase #3.

3. Phase #3 - Decreasing Phase: at higher pressures (above 10 to 12 MPa), the CO2 isotherm decreases rapidly with increasing pressure, and in some cases, trending to zero.

No Scale

Note:

a Concept based on discussion by Busch et al. (2008). Phase #2 is not observed in all tests. The decrease in Phase #3 is substantial and may go to zero. Also, see Type 2 curve defined by Donohue and Aranovich (1999).

**Figure 3: Idealized CO2 sorption isotherm for shale and mudstone.**

The onset of the Decreasing Phase (Phase #3) appears to be roughly coincident with the CO2 phase change from gas to liquid at low temperatures, or the transition from gas to supercritical fluid at elevated temperatures and pressures (above 31 °C). The same type of three-phase
behavior was also noted for ethane (Gasparik et al., 2014), which has a comparable critical pressure and temperature.\(^1\)

The distinct peak response (Phase #2) has been observed by several authors including Busch (2008, 2009), Weniger et al. (2010), and Wollenweber et al. (2010). However, the response is not always observed on mudstones (e.g., Amann, A. et al., 2011), and may and may not be observed by different laboratories on the same material. As reported by Gasparik et al. (2014) on inter-laboratory test comparisons, a Phase 2 response was observed with Namurian Shale by one laboratory, but not by another.

As to representative values of sorption, based on current testing, a typical maximum (peak) value of CO\(_2\) sorption on mudstones is highly variable from the rock to rock, being dependent on several factors. Peak sorption data have been measured over a range of 0.1 to 2.0 mmol/g, at temperatures of 30 to 65 °C and at pressures up to 25 MPa. A peak CO\(_2\) excess sorption of a “typical” mudstone is roughly estimated in the range of about 0.3 mmol/g at 50 °C, which is comparable to the lower range of CO\(_2\) sorption by clay minerals mentioned earlier.

Given the reversal in CO\(_2\) sorption at higher pressures, the relationship of CO\(_2\) to other gases such as CH\(_4\) sorption varies. At pressures below 8 MPa, the excess CO\(_2\) adsorption on mudstones is generally observed to be greater than that of CH\(_4\) at the same pressure. However, above 10 MPa, CH\(_4\) sorption can often be larger, as CO\(_2\) sorption capacity typically sharply declines at higher pressures. For gas mixtures of CO\(_2\) and CH\(_4\), the excess sorption isotherm correlates with the proportions of the CO\(_2\) and CH\(_4\) in the mixture, for pressures less than 10 MPa (Luo et al., 2015; Duan et al., 2016). However, it appears that the trend favors the higher CO\(_2\) isotherm to a small degree. Further, the correlation has not been experimentally investigated at higher pressures (above 10 MPa) where CO\(_2\) sorption on mudstones typically decreases.

2.2.3.2 Other Relationships

As with clay minerals, the CO\(_2\) excess sorption on shales shows a strong inverse correlation with temperature. The relationship appears to be somewhat nonlinear, decreasing with increased temperature. Systematic testing with Qaidam Basin shale has demonstrated an approximately 45% reduction in the CO\(_2\) excess sorption over the temperature range of 35 °C to 85 °C, at pressures up to 12 MPa (Luo et al., 2015). In addition, testing by Duan et al. (2016) indicated a reduction of about 75% in the CO\(_2\) sorption with increasing temperature over the temperature range of 5 °C to 45 °C, at pressures up to 2 MPa on Nanchuan shale. Testing on Dadas shale samples by Merey and Sinayuc (2016) showed an approximately 50% reduction in sorption with increasing temperature over a temperature range from 25 °C to 75 °C.

Based on testing with clay minerals, it is concluded that the CO\(_2\) sorption by mudstones is a function of the total amount of clay minerals and the type of clay contained in the rock unit. Unfortunately, no systematic test program has been conducted to demonstrate this relationship with actual shales as investigations have not focused on this aspect.

\(^{10}\) Ethane has a critical pressure of 4.9 MPa, and a critical temperature of 32.2 °C (NIST, 2016b). Correspondingly, ethane also exhibits a distinct peak in sorption but at a slightly lower pressure than in CO\(_2\).
In addition, testing on mudstones has demonstrated that CO2 sorption is a function of the total organic content (TOC) of the unit. Several authors have proposed a linear relationship of peak sorption with TOC, including Nutttall et al. (2003, 2005), Weniger et al. (2010), Charoensuppanimit et al. (2016), and Hong et al. (2016). Hence, in considering sorption of mudstones, a detailed mineralogical examination needs be conducted together with sorption testing to fully characterize the sorptive material, i.e., both the clay mineral type and clay content, as well as the organic content, must be determined.

Experimental data on the relationship of CO2 sorption to sample water content provide some contradictory trends. From Busch et al. (2008, 2009), an as-received Muderong shale sample (water content 3.34%) exhibited a significantly higher peak sorption value (about 1.0 mmol/g) than a dried sample (at 0.4 mmol/g) at 50 °C.11 However, while the peaks differed, the isotherms for both tests were very similar at lower pressures (less than about 7 MPa).

A similar trend was seen with a sample of Warndt-Luisenthal Shale from Busch et al. (2009) with a moistened sample (9.2% water content) having a peak sorption of approximately 0.35 mmol, while a dried sample had a peak sorption of about 0.15 mmol/g, and with the as-received sample (water content of 0.13%) had an intermediate peak value of about 0.24 mmol/g again at 50 °C. Busch et al. (2009) noted that the response of this sample and the Muderong Shale were atypical, and the “... behavior was unexpected because water and CO2 are believed to compete for the same sorption sites, which should result in lower CO2 sorption capacities for moist samples.”

This is also the reverse of the trend seen with clay minerals by Busch et al. (2008, 2009). In addition, experimental data by Kumar (2016) also shows the reverse trend of decreasing sorption with increased water content. Testing of shale samples from the Bakken Formation showed that the peak CO2 sorption was reduced in samples subjected to pressurized-water imbibition by approximately 40% to 50% in contrast to dried samples a temperature of 50 °C.

It can be suggested that the decrease in peak sorption for the dried shales may reflect a structural change in the samples from Busch et al. (2008, 2009) due to the drying process, which is not reflected in the clay minerals and not present in Kumar’s approach. Further study, however, is necessary to resolve the aspect of water content on whether it increases or decreases peak sorption and under which conditions.

On another topic, there is also little experimental data on the path dependence of CO2 sorption in shales and mudstones. There is a test result by Busch (2008) showing that a second CO2 sorption test cycle evidenced a reduction of approximately 40% in peak CO2 sorption from the first cycle on Muderong Shale. The second cycle isotherm was also comparable to results with a dried sample. The isotherms for these tests were very similar at lower pressures (less than about 7 MPa). Again, additional testing is required to further define path dependence.

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11 The dried Muderong Shale sample and the second loading response of the as-received sample show a dip in the CO2 sorption isotherm at about 10 MPa, which is not seen in other CO2 sorption data.
2.2.3.3 Test Limitations

The test procedures commonly used today preclude an understanding of sorption regarding rock fabric. Sorption tests with mudstones commonly utilize ground (pulverized) samples, and while the pulverized samples expose a large surface area for sorption, the process destroys the mudstone fabric. On the other hand, while the use of intact rock cores in sorption testing could be more representative of in-situ conditions, it requires longer test times considering the low permeability of mudstones. It would also require the development of different test equipment and new test procedures. Related to this issue, it is possible that the grain size of the crushed samples may also influence results, but no correlation of sorption (or lack thereof) is evident in the current data.

In review of the test data in Appendix A.2, it is evident that the procedures for sorption testing and data analyses on shales and mudstones needs further improvement. Negative excess sorption values have been obtained in some tests (e.g., Busch, 2009; Khosrokhavar, 2014), and these negative values are attributed to artifacts in the sorption analysis procedure for CO₂. Further, an inter-laboratory comparison reported by Gasparik et al. (2014) indicated highly variable results for two tested materials with CO₂ by different laboratories and they concluded that the current quality standards of procedures need improvement in measuring the sorption capacity of shales and mudstones.

2.2.4 Observations

To summarize the existing data on the sorption of CO₂ on clay minerals and mudstone:

- The sorption of CO₂ on clay minerals and mudstones shows an atypical-dependence on the gas pressure with a sharp decrease in sorption at higher pressures, potentially influenced by the phase change from a gas to a supercritical fluid.
- The sorption of CO₂ on clay minerals and mudstones decreases with increasing temperature in a somewhat nonlinear fashion.
- The sorption of CO₂ is highly path-dependent on clay minerals, but additional testing with shales and mudstones is required to determine the extent of path dependence with rock.
- The sorption of CO₂ on mudstones is expected to be a function of the type and amount of clay minerals in the rock fabric, but no systematic testing has demonstrated this relationship.
- Several authors have proposed relationships that sorption of CO₂ on mudstones is also a linear function of TOC, with sorption increasing with increased organic content.
- The sorption of CO₂ is influenced by the water content of the sample. It has been suggested that an increased initial water content of the sample will decrease CO₂

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12 There are several possible sources of error that can cause these negative results as discussed in the literature (e.g., Ross and Bustin, 2007; Khosrokhavar, 2014; Gasparik et al., 2014)
sorption. However, as there are contradictory results in the literature, additional testing is required to resolve the type and extent of this dependence.

- Pulverization of samples in sorption tests precludes an understanding of how the mudstone fabric influences sorption.
- Volume deformation is typically not measured during sorption testing, so a volume (swell)-sorption correlation could not be established from the existing literature.
- The accuracy of CO2 sorption tests on mudstones requires further improvement given the large variation in sorption data on the same sample by different laboratories (seen in interlaboratory testing comparisons) and the presentation of negative data values in the literature.

2.3 CO2 INDUCED VOLUME CHANGE - SWELL

2.3.1 General

Many clay minerals and some mudstones will expand significantly in volume (swell) when the applied stress is reduced and the material is then exposed to a source of H2O/groundwater, as discussed by Lindner (2016b). Clays and mudstones can also swell when exposed to CO2 in this manner, but the response is more complex as CO2 does not replace existing H2O in the clay mineral structure but rather interacts with it. Under the proper conditions, CO2 can be sorbed by the wetted clay mineral structure, potentially inducing swell of the material. Under other conditions, a predominate CO2 fluid can draw H2O out from the clay mineral structure, effectively drying the material, which in turn can induce a decrease in volume (shrinkage).

There is only a limited available amount of data on swell testing with larger lab-scale or bench-scale sized samples, so most of the discussion examines microscopic test results which must be conceptually extrapolated to be representative of field behavior. In reviewing these data, it is understood that CO2-brine-rock interactions are the actual focus of the investigation, not just the simple exposure to CO2 alone, and that the range of CO2-brine mixtures in the field can range from mixtures of H2O dissolved in CO2 to CO2 dissolved in H2O and that the brine can incorporate a range of dissolved salts, which will impact the amount of swell.

Available experimental data on the effect of CO2 on clay and mudstones are summarized in the following sections, focusing first on clay mineral behavior and then in subsequent sections, examining the response of mudstones.

2.3.2 Clay Mineral Microfabric Response to CO2

A number of tests on the expansion and contraction of clay mineral samples have been conducted since 2012 (See Appendix B.1). Most of this testing has been on small quantities of crushed montmorillonites exchanged with different cations (potassium (K), calcium (Ca), sodium (Na)) and measured using X-ray diffraction (XRD) and similar methods. Swelling in this context is described in terms of the inner layer basal spacing (d_{001}), expressed in Angstrom (Å) or in
spacings for the hydration states of the clay mineral (0W, 1W, etc.). For most this testing, “standard” mineral samples were obtained from the Clay Minerals Society.\textsuperscript{13}

This testing demonstrated that CO\textsubscript{2} interacts with clay minerals and that a volume change in the clay microfabric (either swell or shrinkage), when it occurs, is observed to depend on the initial interlayer spacing. As discussed by Busch et al. (2015), molecular dynamic studies using density functional theory have demonstrated that CO\textsubscript{2} can intercalate the clay mineral interlayer resulting in volume expansion. However, the interaction is complex, and swelling/shrinkage is dependent not only on the initial water content (i.e., interlayer spacing), but also on CO\textsubscript{2} intercalation reactions. Loring et al. (2013) concluded that “… these processes are controlled by the amount of water dissolved in the scCO\textsubscript{2} at a given temperature and pressure.”

In more detail, there are various aspects to the swell or shrinkage behavior due to CO\textsubscript{2}. Like sorption, the amount of swell is dependent on clay mineral structure, with the swelling of montmorillonites is greater than that of kaolinites (Loring et al., 2014). In addition, the amount of swell is dependent on the exchanged ion of the clay, as the swell of Ca-montmorillonite has been observed to be greater than Na-montmorillonite under similar conditions, which in turn is comparable to K-montmorillonite, (Giesting et al., 2012b). The response is also considered rapid.

The amount of swelling when exposed to CO\textsubscript{2} is related to the initial inner-layer spacing of the clay mineral (hydration) and appears restricted to more “wet” samples (i.e., increased water content/interlayer spacing). For example, as observed by AlOtaibi et al. (2012), Na-montmorillonite samples with a spacing of 11.67 Å swelled 60.4% when exposed to CO\textsubscript{2}. However, air-dried samples (i.e., with minimal spacing) soaked in CO\textsubscript{2} for 24 hours did not swell appreciably. Similarly, Giesting et al. (2012a) noted that significant expansion occurs in Na-montmorillonite exposed to CO\textsubscript{2} when the initial basal spacing values are between 10.0 and 11.5 Å, but little expansion is observed below this range (0W), and no expansion is observed above it (1W). Tests on dried samples of Ca-montmorillonite and Na-montmorillonite by AlOtaibi et al. (2012) also showed no expansion when exposed to scCO\textsubscript{2} alone.

On this topic of initial inner-layer spacing affecting response to CO\textsubscript{2}, Busch et al. (2016) summarized several test results on differing montmorillonites, shown in Figure 4. Both swell and shrinkage are observed, together with ranges of little-to-no response with CO\textsubscript{2} exposure, varying with initial water content.\textsuperscript{14} The data suggest that the peak response occurs at an initial d\textsubscript{001} spacing of about 1.11 ηm, and is at a minimum at the bounds for the region of 0W and 1W (0.96 ηm and 1.25 ηm on the diagram). As noted by Schaef (2015), these data indicate that CO\textsubscript{2} can only enter the interlayer space when the clay structure is already propped-open after a minimum concentration of H\textsubscript{2}O is present, i.e., above the 1W bound. Further, Giesting et al. (2012b) suggested that the expansion of Na-montmorillonites is limited to occur within the 0W to

\textsuperscript{13} A list of the symbols used for standard montmorillonite and other clays are provided in Appendix A; the physical and chemical data for these standard samples are described by CMS (2016b).

\textsuperscript{14} The variable water content is described using the initial d\textsubscript{001} spacing of the clay. Also, note that the hydration states (0W, 1W, etc.) implied by the colored zones shown in the figure can vary (to some degree) with the specific type of montmorillonite, and the reported bounds do vary in the literature.
IW region, but Ca-montmorillonites expansion can occur within 0W to 2W bounds, which is consistent with the data with Figure 4.

![Figure 4: Summary of the change in inner layer spacing in montmorillonite samples after exposure to CO2 from Busch et al. (2016).](image)

Source: Busch et al. (2016)

Note:

- Designations SWy-1, SWy-2, STx-1 are from the Clay Minerals Society; see Appendix A.
- 1 Å = 0.1 nm.

This swell response also appears to be pressure dependent. Giesting et al. (2012a) noted that swell increases with pressure but the amount of swell ceased above 5.0 MPa and de Jong et al. (2012, 2014) also saw no significant change at higher pressures (above 7 or 15 MPa respectively). Others have made no direct mention of a pressure limit, but this pressure dependence could correlate to the transition from CO2 gas to scCO2 and with the corresponding decrease in sorption as described in Section 2.2.2.

The swell response to CO2 also appears to be largely reversible when test conditions are returned to the initial state. Testing by Schaeff et al. (2012) indicated a full recovery of the volume increases due to CO2 upon depressurization and vacuuming, with spacings returning to their original positions and intensities. Testing by de Jong et al. (2014) indicated only insignificant strains remained after testing and dehydration of the sample. However, data by Giesting et al. (2012b) indicates that in simply depressurizing the sample at the end of the test, the sample does
not fully recover the strain and that some swell strain is retained. This indicates that under field conditions, some hysteresis in response can be expected.

Some temperature-dependence of swell can be suggested, but it is undefined at present and no systematic testing has been performed.\textsuperscript{15}

In contrast to swell response, testing has also shown that shrinkage can occur at higher initial clay mineral saturations ( spacings at $2W$ and $3W$) with (anhydrous or dry) scCO$_2$. Tests by AlOtaibi et al. (2012) showed that for samples first soaked in distilled water and then exposed to scCO$_2$ (samples with a spacing at about $18.7$ to $18.8$ Å), the resulting d$_{001}$ spacings decreased (contracted) 25% and 60.4% for Ca-montmorillonite and Na-montmorillonite, respectively. The authors also stated that the samples had an apparent drying effect due to this exposure.

Dehydration tests by Ilton et al. (2012) with scCO$_2$ with partial H$_2$O saturation (i.e., wet scCO$_2$) also showed a drying effect on clays at a higher water content. Partial dehydration effects were noted on $3W$ to $2W$ clays, showing a volume loss on the order of 15% depending on the initial spacing. As noted by the authors, dehydration can occur with scCO$_2$ at H$_2$O saturations as high as about 31% for $2W$ clays and about a 64% saturation for $3W$ clays.

Schaef et al. (2015) also observed this type of dehydration with Ca-SWy-2, as well as with Ca-STx-1, Na-SWy-2, and magnesium (Mg)-SWy-2. Schaef et al. (2015) concluded that “…scCO$_2$ can either diffuse into or extract H$_2$O from the interlayer region of montmorillonites to produce volumetric changes.” They proposed that the clays with the higher inner layer spacings (of $2W$ and $3W$) released some H$_2$O from the clay to wet scCO$_2$,\textsuperscript{16} resulting in a reduction in volume.\textsuperscript{17}

The response of the clay is also influenced by the H$_2$O saturation of the scCO$_2$ used in testing. Loring et al. (2013) tested Ca-montmorillonite exposed to scCO$_2$ as a function of the percent H$_2$O saturation of CO$_2$ over a range of 0% to 40%. Their results indicated that increasing concentrations of intercalated water (i.e., increasing H$_2$O saturation) led to decreasing concentrations of intercalated CO$_2$ in the sample.

In summary, several aspects have been identified on CO$_2$ volume interactions, but more research is required. Overall, the total amount of volumetric strains due to CO$_2$ exposure has been moderate to large but restricted by the hydration of the clay mineral. As noted by Busch et al. (2016), research involving clay mineral sorption and swelling (and the potential consequences for CO$_2$ storage containment) “is still quite immature and requires further work.” While considering diffusive transport in the caprock not to be significant, they note that smectite-bearing shale could be dewatered by “…pore or interlayer water dissolution in CO$_2$. As a consequence, dehydration cracks are plausible…”

\textsuperscript{15} Spiers (2015) illustrated test results with smectite showing that swell decreases to a limited degree with increasing temperature. Spiers also stated that swell decreases with increasing effective stress and decreasing water content. However, no test data were provided in support of these statements.

\textsuperscript{16} Except in cases where the scCO$_2$ was oversaturated with respect to H$_2$O where dehydration does not occur.

\textsuperscript{17} The process may involve the replacement of H$_2$O in the clay structure by CO$_2$, but this concept disagrees with analyses by Loring et al. (2014).
2.3.3 **Lab Scale Response of Clay Minerals to CO₂**

Little testing on larger size clay samples for CO₂-induced swell is reported in the literature, and only two sets of experiments were found on samples more than a few millimeters in size (these tests are described in more detail in Appendix B.1).

The first set of tests is described by Heller (2013) (also reported by Heller and Zoback, 2014). The author conducted lab-scale triaxial swell tests on kaolinite, illite, and mature kerogen samples. For swell tests, the source materials were ground and formed into samples 25 mm in diameter and 50 mm in height and were tested at a temperature of 25 °C in a triaxial test apparatus. The samples were dried prior to testing and subjected to a series of consolidation loads. For each swell test, the sample was exposed to a series of step-wise, increasing pore pressures at a constant effective stress and the swell recorded after a few hours.

Results of this testing indicated only very small amounts of swell for all three samples upon exposure to CO₂ gas. Volumetric swell was only about 0.03% to 0.08% upon exposure to CO₂ for kaolinite, and 0.04% to 0.17% for illite. Volumetric swell with kerogen exposed to CO₂ was somewhat higher, ranging from approximately 0.03% to 0.55%.

Using a separate set of sorption tests, Heller and Zoback (2014) constructed a swelling/sorption diagram for exposure to CO₂ and CH₄ gases. The resulting diagram suggests a correlation of increasing swell with increasing sorption for clay minerals, as shown in Figure 5. However, it is noted that this correlation must be considered to some degree tentative, as the sorption data were taken during a separate set of tests at 40 °C on crushed samples, and then curve fit to obtain sorption values at the same pore pressure values in the swell tests, as reported by the author.

The second set of tests is reported by Zhang et al. (2013, 2014). These authors conducted several 1-D swell pressure tests with Na-montmorillonite exposed to scCO₂. Samples were compacted into a consolidometer with a diameter of 12 mm and a thickness of about 0.7 mm, consolidated and then exposed, under pressures to scCO₂. Starting (external) test pressures ranged from 10 MPa to 30 MPa, and tests were conducted at temperatures from 44 °C to 80 °C.

Swelling pressures measured during this program evidenced values from 5 to 11 MPa with stresses decreasing with increasing applied load and decreasing with increasing temperature. Figures provided by Zhang et al. (2013) for tests at 44 °C and 50 °C indicate that the trends were generally linear in nature but with one sample showing high variability.
2.3.4 Swell Response of Shale/Mudstones

Based on limited testing of mudstone samples with CO₂, the swell due to CO₂ shows similar trends to the hydration response of shales and mudstones, as described by various authors (e.g., Lindner, 2016b), but at reduced strain or pressure. For example, hydrostatic swell tests\(^{18}\) on dried

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\(^{18}\) Typical test methods and typical apparatus briefly described in Lindner (2016b). In this case, however, while the test was not unlike a free-swell test, it was conducted under hydrostatic pressure in a pressure cell. While termed a “hydrostatic swell test,” it is technically a variant of the triaxial swell test.
samples by Choi and Song (2012) indicate varying response of shale due to exposure to different fluids. In this testing, the samples (38 mm in diameter and 70 mm in height) were subjected to a hydrostatic pressure of 10 MPa and were tested at a temperature of 80 °C to 100 °C; samples were exposed to water, brine, scCO₂ alone, scCO₂ plus water, and scCO₂ plus brine.

As observed in this testing, the axial swell of shale was greater with scCO₂ alone than it was with either brine or water alone. Adding pure water to scCO₂, the swell increased, but the swell of the sample exposed to scCO₂ and brine was substantially less than either the sample exposed to scCO₂ alone or the sample with scCO₂ and water. In review, the final swell with scCO₂ and brine was on the order of that with water alone. However, in all test cases for these authors, the amount of swell was very small and the maximum axial displacement was less than 0.12 mm (about 0.17% strain) over a two-week exposure period.

Swell testing with mudstones has also indicated that swell due to CO₂ exposure decreases with temperature, and increases with gas pressure at lower pressures. Hydrostatic swell testing of dried mudstones with a small clay content (less than about 16%) over a range of 35 °C to 75 °C were performed by Lu et al. (2016) with samples having a diameter of 50 mm and a height of 100 mm. These tests indicated a decrease of 35% in volumetric swell strains observed over a range of pressures, as shown in Figure 6. Also evident in this figure at low pressures (less than about 8 MPa), there is an asymptotic increase in swell with increased cell pressure; but above this pressure, little pressure dependence is seen. Again, the magnitude of volumetric swell in these tests was very small, less than 0.17% in all tests. The swell in these tests also occurred relatively rapidly, reaching an approximate asymptotic value within about a day or two.

To highlight the complexity of response from CO₂ exposure, tests on small rectangular samples of Marcellus Shale by Zhao (2015) indicated that the sample decreased in area after the initial exposure to CO₂ gas at low pressure (i.e., less than 0.7 MPa), and then exhibited expansion at 2 MPa and at subsequent pressure increases up to 5 MPa.

Unfortunately, no other lab scale swell tests conducted with CO₂ were found in the literature. This necessitates any general discussion on the topic to rely solely on microfabric testing with clay minerals, which is unsatisfactory, and there is an apparent research need for additional testing in this area. Further, there are also reports in the literature where CO₂ exposure produced no observed swell in shale samples (e.g., Markiewicz, 2014; Bacon et al., 2015), and defining the conditions under which CO₂-related swell does (and does not occur) is mandatory in making long-term predictions as required for geologic sequestration.

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19 The authors described the samples as shales, but provided no details on the source, or clay content of the material.

20 Description of the how the water was purified was not provided by the authors.

21 Samples were approximately 3 x 3 mm in area and about 2 mm thick.

22 For definition of lab scale size, see Lindner (2016a).
Some of the more important aspects of the swell/shrinkage behavior after exposure to CO2 are:

- Microscopic testing on montmorillonites has demonstrated a range of swell/shrinkage response upon exposure to CO2 by many authors.
- The swell/shrinkage response of clay (montmorillonites) is strongly dependent on the initial water content (hydration state) of the material. Ranges of hydration states where no swell/shrinkage occurs have been observed in testing (see Figure 4).
- The swell/shrinkage response of clay (montmorillonites) is also strongly dependent on the initial degree of saturation of the CO2-H2O used in testing.
- Lab-scale testing of compacted samples of kaolinite and illite show little response to CO2, based on limited testing (e.g., Heller, 2013). Similarly, microscopic testing with kaolinite had indicated only a small response (Loring et al., 2014).
- The swell response of clay minerals upon exposure to CO2 is not completely reversible unless the moisture content is restored to the original value, based on limited testing.
- The swell of a shale saturated in brine and then exposed to scCO2 is substantially less than the same shale saturated with distilled water and scCO2 (Choi and Song, 2012).
is analogous to hydration swell of shale, which is also dependent on the salinity of the wetting fluid (e.g., see Lindner, 2016b).

- As mentioned by Zhang et al. (2014), the swell of montmorillonite decreases with increasing temperature and increases with increasing water content in lab-scale samples. Similarly, the swelling of mudstones due to CO$_2$ exposure decreases with increasing temperature (Lu et al., 2016).

- The observed swell of mudstone and shales due to CO$_2$ exposure is generally very small, less than approximately 0.2% based on current limited lab-scale testing. However, lab scale tests have not investigated the potential of mudstones with higher clay mineral content (i.e., research shales) or with clay minerals that swell significantly (i.e., smectites and mixed-layer clays) and additional work is required to define typical amounts of swell.

- Laboratory test data suggest that there is a potential for shrinkage of shale due to the removal of H$_2$O (i.e., dryout) (and possibly due to replacement by CO$_2$). This shrinkage, in turn, can induce fractures in the caprock under appropriate conditions, leading to increased permeability in the caprock. Additional research is needed to define the extent of the potential for desiccation of clay minerals due to H$_2$O dissolution in dry scCO$_2$ at typical conditions for sequestration.

- Overall, there is a lack of data on this topic. A systematic examination of CO$_2$-induced swell at the lab-scale$^{23}$ (under free swell or applied stress conditions) has not been conducted. Simply stated, additional testing is required to fully characterize the swell/shrinkage response of both clay minerals and mudstones when exposed to CO$_2$ and brine.

- There is no demonstrated experimental correlation of swell with sorption, although some analyses have suggested trends with clay minerals. Additional experimental equipment development is required to perform tests that will measure both aspects concurrently and accurately in the same test.

- The testing of clay mineral structure due to CO$_2$ exposure using XRD methods has focused on montmorillonites, and a systematic examination of other clay minerals is lacking.

- On a conceptual basis, it is important to note that the testing of clay minerals (which have been sorted, dried, and crushed) cannot be expected to accurately reflect the response of shales at natural water content and an (intact) heterogeneous microfabric in the field.

- Further, given the potential factors that could influence swell, the extrapolation of microscopic-scale testing results on clay minerals to the large-scale response of shales is open to question.

$^{23}$ Scale definitions provided in Lindner (2016a).
2.4 CHEMICAL REACTIONS AND pH CHANGES WITH CO2

2.4.1 General

A number of chemical reactivity tests have been performed to examine the chemical effects of CO2 exposure on shales and mudstones (see Appendix C). Often, these tests are performed in a special pressure cell or batch reactor (e.g., as discussed by Kaszuba et al., 2013), are pressurized with CO2 gas and the test fluid is sampled regularly for ion or elemental concentrations. Exposure durations have ranged from 2 days to 1,814 days (or approximately 5 years), and these data extend over a range of pressures from atmospheric up to 20 MPa and temperatures ranging from room temperature to 250 °C.

Geochemical reactions due to CO2 exposure include mineral dissolution, mineral transformation and secondary mineral formation and precipitation. From experimental data, it is evident that chemical processes with CO2 and brine on mudstones are dominated (at least initially) by acid-induced dissolution. These reactions are due to the combination of CO2 and groundwater (brine) forming an acid (carbonic acid, H2CO3), which disassociates and induces low pH, and in turn initiates other chemical reactions and alterations.

Simply, this dissolution of CO2 in water can be expressed as (e.g., Wawersik et al., 2001; Gaus, 2010):

\[
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-
\] (1)

Although a large portion of CO2 will not react with water, and the formation of the acid is relatively slow, the final dissolution of the reaction is rapid and can occur within 24 hours as kinetics demand. The dissolution of the acid will decrease the pH (to levels of roughly 5 or less), which will allow interactions with minerals present in the mudstone.

The acid will stimulate dissolution, with the hydrogen ion reacting with existing carbonates, placing minerals in solution and buffering the acid. A reaction with calcite or siderite will involve:

\[
\text{CaCO}_3 \text{ [calcite]} + \text{H}^+ \rightleftharpoons \text{HCO}_3^- + \text{Ca}^{2+}
\] (2)

or:

\[
\text{FeCO}_3 \text{ [siderite]} + \text{H}^+ \rightleftharpoons \text{HCO}_3^- + \text{Fe}^{2+}
\] (3)

This dissolution, dominant with a higher concentration of carbonic acid, can open mineral-filled fractures in a rock mass, enhancing permeability.

24 The terms brine and groundwater are used interchangeably in this context as groundwater used in many engineering applications at depth will be highly saline, and laboratory testing often uses a simple saline solution (brine) to represent groundwater. Groundwater at depth contains various salts, minerals and trace elements, which are not discussed here.
There can also be reactions inducing feldspar dissolution, such as under high Na⁺ concentrations (e.g., Johnson et al., 2004):

\[
KAlSi_3O_8 [\text{feldspar}] + Na^+ + CO_2(aq) + H_2O \rightleftharpoons NaAlCO_3(OH)_2[\text{dawsonite}] + 3SiO_2[\text{silica / chalcedony}] + K^+ \tag{4}
\]

Feldspar can also transform in an acidic environment as (e.g., Wdowin et al., 2014):

\[
2KAlSi_3O_8 + 2H_2CO_2 + 9H_2O \rightleftharpoons Al_2Si_2O_5(OH)_4 [\text{kaolinite}] + 4H_4SiO_4 [\text{silicic acid}] + 2HCO_3^-[\text{bicarbonate}] + 2K^+ \tag{5}
\]

As the overall solution travels through the rock, it becomes buffered; reactions with other minerals can form secondary minerals, as in the creation of various carbonates, i.e., (e.g., Johnson et al., 2004):

\[
Mg^{2+} + CO_2(aq) + H_2O \rightleftharpoons MgCO_3 [\text{magnesite}] + 2H^+ \tag{6}
\]

This reaction (and the reverse reactions of Equations 2 and 3) result in precipitation into fractures and pore space, which can isolate pores and seal fractures, reducing rock mass permeability.

Feldspar can also combine with Mg-chlorite to form muscovite, kaolinite, and magnesite (e.g., Johnson et al., 2004):

\[
KAlSi_3O_8 + 2.5MgAl_2Si_3O_10(OH)_8 [\text{Mg-chlorite}] + 12.5CO_2(aq) \rightleftharpoons KAl_3Si_3O_10(OH)_2 [\text{muscovite}] + 1.5Al_2Si_2O_5(OH)_4 [\text{kaolinite}] + 12.5MgCO_3 + 4.5SiO_2 + 6H_2O \tag{7}
\]

As noted by Johnson et al. (2004), the last reaction occurs with an 18.5% volume increase.

These foregoing reactions are just a few of the possible processes that can occur with CO₂ exposure. They can either enhance or degrade the permeability of the rock mass. Given the range of possible combinations and varying conditions, the reactions that occur in situ are governed by the mineralogy and chemistry of the rock unit as well as in situ conditions, together with the existing groundwater and the characteristics of the injected CO₂. The chemical processes are also highly transient and therefore, reactions are time-dependent and location-dependent as well.

In a rock mass, the chemical reactions are also coupled to pressure response as the physiochemical reactions will induce swell pressures, as described in the previous section, which will limit porosity and close fracture apertures. These changes will redirect and limit flow paths, thereby affecting the CO₂ ingress and restricting reactions. In addition, mineral alteration may be accompanied by volumetric changes (swell or shrinkage) creating pressures within the rock material, which in turn (again) change flow path characteristics and influence reactions.
2.4.2 Experimental Results

2.4.2.1 Significant Chemical Changes from Various Sources

As a generalization, the predominant chemical reactions that occur with mudstones (and in particular, shales) are difficult to identify due to the possible range of chemical reactions and due to the lack of description of the mineralogy of tested samples in the literature. Further, many authors use different base solutions for testing, ranging from distilled water to brines (with a range of salt content), making comparisons even more tenuous. However, to generally characterize CO₂ reactions, the most significant changes in chemistry are reviewed in this section based on test results with mudstones and CO₂ available in the literature.

From the data, reactions of the initial test fluid alone (i.e., brine) with the rock sample can be an influential factor in chemical testing and results. For example, the reference brine developed by Credoz et al. (2009) was noted to significantly react with the mudstone samples. The fluid had a pH 6.3 and was formulated with standard laboratory grade salts. Reaction with this fluid caused significant chemical reactions including significant increases in Ca and K concentrations at 80 °C and strong decreases in Mg at 150 °C together with an increase in Na. In situ, it is expected that the rock mass will be saturated, and essentially in equilibrium with the existing pore fluid away from injection borings. Therefore, the discussion in this section is focused on the changes due to CO₂ from conditions of rock first reacted with brine rather than from chemical reactions of combined CO₂ and brine on unreacted rock.

Initial reactions of CO₂ with brine and mudstone are dominated by dissolution of carbonates and the subsequent precipitation elsewhere. Czernichowski-Lauriol et al. (1996) observed in their testing at 80 °C the significant dissolution of dolomite and the possible precipitation of Mg, iron (Fe), potassium aluminum silicate, and secondary calcite. This alteration and the associated increase in porosity was not always evident on the sample surface, but was more evident with water alone. Also, the processes weakened the fabric of the rock, as the rock samples disintegrated into fragments at the end of testing.

Clay minerals in the rock can also be altered in the process. Busch et al. (2009) examined CO₂ exposure at 50 °C and 15 MPa over 32 days with shale and water in a batch reactor. They recorded a significant increase in smectite together with a corresponding sharp decrease in illite content in their tests, suggesting a transformation from one clay mineral to another. There was also a significant increase in feldspar, a moderate decrease in siderite and relatively very minor changes²⁵ in quartz, pyrite, chlorite, and kaolinite.

Further, a variety of changes in brine geochemistry with the introduction CO₂ has been observed over a range of conditions for durations on the order of months. Some major examples include:

Kaszuba et al. (2003) at 200 °C observed the significant increase in Fe, and a moderate increase in Cl and SiO₂ together with a moderate decrease in Na and Br in solution after CO₂-brine reactions. pH in these experiments ranged from 4.7 to 5.8. Tests by Kaszuba et al. (2005) at 200 °C also noted significant decreases in Na and Cl, and increases in Fe,

²⁵ Considered to be within the experimental error by the authors.
manganese (Mn), and Mg$^{2+}$ at pH approximately 4.1. Precipitation of carbonate minerals, siderite, magnesite crystals together with secondary clay minerals was observed with shale-arkose rock.

Testing from Credoz et al. (2009) at 80 °C for 30 days indicated significant increases in Ca and Mg in both mudstone samples and a significant increase in Na in one sample with scCO$_2$ and brine. At 150 °C, this response is more muted, although Mg response is similar (but stronger considering the starting concentration). The response to CO$_2$ dissolved in the brine is also minor compared to scCO$_2$. However, with the aqueous CO$_2$ at 150 °C, the authors observed the formation of a Fe-Mg smectite, the dissolution of kaolinite and the destabilization of the mixed smectite-illite minerals resulting in an illitic-mixed-layer. Pyrite was also noted as massively dissolved in the aqueous CO$_2$ at 150 °C. In addition, reactions of aqueous CO$_2$ at 150 °C over 45 days with various clay minerals showed relatively small increases in Ca and Mg together with a large decrease in Na.

Results from Kohler et al. (2009) (at 150 °C and a pressure of 15 MPa over a period of 30 to 60 days) showed decreases in carbonate content and in the clay minerals of samples together with sharp decreases in anhydrite/pyrite with exposure to CO$_2$ and water. Quartz content increased, however in this test. Samples exposed to CO$_2$ showed a clear illitization of the clays, with the transformation of Fe-chlorite to illite, and increases in mixed illite-smectite. The authors concluded that the overall process could lead to increased porosity and increased plasticity of the sample.

Carroll et al. (2011) exposed Krechba Field Shale to a scCO$_2$-brine solution for 31 days at 95 °C. This testing showed a significant increase in Fe concentration, and a moderate increase in Si and a small increase in Al during the period, with little change in Mg or Ca. Scans showed little indication of alteration of the shale but some precipitation was noted on the surface. Carroll et al. (2013) performed similar tests with Eau Claire Shale at 51 °C with brine CO$_2$ solution for 30 days. This testing showed a significant increase in Fe concentration, and a moderate increase in Al and a small increase in Si during the test, with little change in Mg or Ca. Significant alteration of the shale was not observed but some precipitation was noted on the surface.

Similarly, results of CO$_2$-brine and -rock reactions from Liu et al. (2013) (reacted for 29 days under 30 MPa pressure at 200 °C) showed minor corrosion of feldspar and anhydrite surfaces, together with the precipitation of secondary minerals in the samples including illite and/or smectite, and siderite near pyrite. Significant changes also occurred in concentrations with increases in of Ca, and N, and decreases in Si, oxygen (O), and Al.

The mineralogy of the shale can be a major determinant in chemical reactions. Testing of two shales, one carbonate-rich, and the other clay-rich can show different reaction results, as described by Alemu et al. (2011). The authors note that the carbonate-rich shale was more reactive at 250 °C, exhibiting dissolution of plagioclase and clay minerals (illite and chlorite), dissolution and re-precipitation of carbonates, and the formation of smectite, after exposure to scCO$_2$ and brine for 35 days. There were marked increases in K and silicone (Si) and a significant decrease in Al over the exposure period. In contrast, the clay-rich sample did not show a significant dissolution of illite and chlorite (or the formation of smectite). Moreover, the clay-rich sample did not show any significant formation of carbonates over the temperature
range of 80 °C to 250 °C. In addition, the clay-rich sample exhibited a sharp decrease in the concentration of K with a significant increase in SiO₂ concentration. There were also moderate decreases in Mg and Ca as well as minor increases in Fe and Al.

Along similar lines, experimental data from Miller et al. (2016) also showed differing response with two shales when exposed to CO₂-saturated brines at 160 °C for approximately 45 days. With one mudstone, the Fe concentration increased throughout the test duration, and both SiO₂ and SO₄ exhibited an initial spike in concentration with SiO₂ remaining relatively constant thereafter but SO₄ decreasing to levels below the initial concentration. Minerals such as anhydrite and gypsum decreased initially and then reached equilibrium, while Ca, dolomite, and magnesite decreased then increased and then made a sharp decrease just before the end of testing. The second shale (with higher carbonate content and probably higher clay content) showed a variable Fe content over the test, with other concentrations (including SiO₂ and SO₄) remaining relatively stable. Minerals such as anhydrite and gypsum were initially relatively stable, but then exhibited increased variability and a sharp increase at the end of testing. The concentrations of other minerals (including anhydrite, gypsum, quartz, chalcedony, cristobalite, tridymite, and amorphous silica) were relatively stable over most of the test duration but also showed an abrupt increase at the end of testing as well.

Work by others (as described in Appendix C) exhibit comparable results to the foregoing, over a range of conditions, including the dissolution of carbonates, the precipitation of secondary minerals, and the alteration of clay minerals often occurring in samples.

Briefly, to summarize these results:

- Garrido et al. (2013) showed a decrease in SO₄ together with significant increases in HCO and Si (which were both absent before testing). Testing was conducted at 53 °C with CO₂ and brine over a period of 60 days.

- Testing by Lahann et al. (2013) with CO₂ and water indicated little alteration and dissolution with some possible minor oxidation of pyrite at 150 °C. The concentration of Ca tended to increase, while Mg and K concentrations decreased at low pressure. In addition, Ca and Mg tended to increase with pressure, but K concentration remains practically constant up to pressures of 24 MPa. The Fe concentration was also occasionally elevated. Test durations varied up to 21 days.

- Wdowin et al. (2014) tests exhibited significant increases in the concentrations of HCO₃, Mg, K, and SO₂ with claystone samples upon exposure to CO₂. There was also a minor decrease in Ca, and relatively small increases in Na and Cl. Wdowin et al. also observed precipitation of poorly developed kaolinite crystals. Tests were conducted with brine at room temperature for 18 months at 6 MPa.

- Data from Edlmann et al. (2016) showed significant increases in the weight of illite and gypsum along with major declines in muscovite, quartz, and K-feldspar. There were also moderate decreases in calcite, kaolinite, ankerite, and pyrite as well as a moderate increase in dolomite. The samples were subjected to “cook and look” tests with samples immersed in a CO₂-saturated brine at 55 °C for 3 months at ambient pressure.

- Relatively short duration tests (up to 5 days) exposing shales to scCO₂ (only) were performed by Jiang et al. (2016) over a range of temperature from 40 °C to 90 °C. In response, the samples exhibited dissolution of minerals and extraction of organic matter.
Post-test analyses indicated a significant increase in Si in the sample, and significant decreases in Ca and Mg. There was also a small decrease in O and an increase in C.

- Szabó et al. (2016) conducted experiments on three samples from the same formation with CO2 and brine at a temperature of 180 °C. They noted that the changes in ions were similar but not uniform. The authors also observed a shift in the illite/muscovite content towards mixed-layer illite/smectite and then to smectite content. Data also suggested a moderate dissolution of quartz and indicated the dissolution/precipitation of carbonate minerals. Chemically with exposure, there are significant increases in Fe and Mg in two of the samples, and an increase in Al with one sample. In general, there were increases in SiO2, Mg2+, Al3+, K+ and Fe_{total} concentrations with CO2 exposure. Exposure time varied from 28 days to 57 days.

- Tests by Wang et al. (2016) over 12 days at 160 °C with CO2 and brine evidenced significant increases in Mg and Ca together with smaller changes in Si, K, and Fe. The brine was saturated with respect to kaolinite, quartz, and smectite with CO2. The precipitation of carbonate minerals was observed, and the authors concluded that dissolution of calcite and illite/smectite and the formation of dolomite, siderite, illite, and chlorite had occurred.

- Yin et al. (2016) conducted tests on shales with scCO2 for 30 days at a nominal temperature of 40 °C. Analysis of the samples after testing indicated that the dissolution of some organic matter and mineral components (such as montmorillonite, kaolinite, and calcite) had occurred. SEM analysis showed minor surface alteration and the narrowing of macropores and micro-cracks.

In summary, mudstones show a wide range of response and all mudstones do not react to CO2 in the same fashion. The reactivity of shale to CO2-brine is highly dependent on the mineral composition of the rock as well as the existing brine.

Nevertheless, throughout this testing, there are a few consistent threads. In many cases, short-term, CO2-brine-rock reactions induce an increase in Fe and Mg concentrations in the brine, and sometimes Si (SiO2) and Al as well. Longer term reactions show increases in Fe, Al, and NO3 with time. Clay mineral dissolution, transformation, and precipitation have been observed in many cases and occur across a wide range of temperatures (25 °C to 250 °C). These data suggest the clay transition progresses from chlorite to illite, to mixed illite-smectite and eventually to smectite, but the precise reaction path is not well defined.

### 2.4.2.2 Enhanced Reactivity with Water

The presence of water or brine with scCO2 influences reactivity with rock and the absence of H2O can inhibit alterations due to CO2. Reactive test data by Czernichowski-Lauriol et al. (1996) with scCO2 alone over a period of 8 months indicated that a mudstone sample appeared unreacted and no secondary porosity was noted on the surface. (This testing was performed at a temperature of 80 °C and a pressure of 20 MPa.) In another case, Czernichowski-Lauriol et al. observed that the partial submergence of a mudstone sample in a seawater brine and exposure to scCO2 for a period of 3 months induced surface porosity but only on the submerged portion of the sample. In contrast, the “dry” upper portion of the sample (exposed only to scCO2 alone) showed little change. Increasing the exposure duration on a partially-submerged sample from
3 to 8 months, however, showed that alteration now occurred over the entire sample with secondary porosity apparent over all surfaces (i.e., on both wetted and dry portions).

Further, as documented in Appendix C, reaction with CO₂ and brine in several test programs can occur in a matter of days. As stated by Bryan et al. (2013), “… wet scCO₂ is more reactive and that reactivity is a function of water content in the scCO₂ phase.” They also concluded that only a small quantity of water may be needed to enhance reactivity with CO₂, such as from rock adsorption and capillary condensation (Bryan et al., 2013).

**2.4.2.3 Reaction Rates with Time**

Reactivity is also affected by exposure duration. In experimental data, the rates of reaction processes with CO₂ on mudstone show distinct trends with time. Starting with the introduction of CO₂ in an experiment, various geochemical changes start almost immediately but quickly reach equilibrium or stability within the first few days of testing. For example, Kohler et al. (2009) described initial reactions with CO₂ and brine as surprisingly rapid.²⁶ Busch et al. (2009) reported changes in the minerals occurred in the period between 6 and 10 days after CO₂ injection and most of these minerals only changed little thereafter. Results from Carroll et al. (2011) showed little change in most minerals and elements (Si, Mg, Al, Ca) in solution after about 6 days, except for Fe.

After the initial sharp change in concentrations, reactions show little change over longer periods of time for the most part. For example, observations by Liu (2013) indicated significant changes in reaction rates were evident at early times (at less than 23 days), but with little change in concentrations of N, Fe, Na, Ca, K, and Al thereafter to 42 days. Similar results are shown by Miller et al. (2016) with steady rates for most ions after 19 days to 45 days.²⁷ Results from Alemu et al. (2011) show relatively gradual rate changes during 7 to 35 days of exposure²⁸.

However, some reactions with CO₂ and brine continue to occur at later times. Concentration monitoring over extended periods of up to 1,814 days (approx. 5 years) by Bateman et al. (2013) shows significant variations in concentrations of NO₃, Fe, and Al over the entire test period, while other elements and compound concentrations remain relatively constant (see Figure 7). XRD analysis also indicated a significant decrease from the unreacted caprock in calcite and chlorite in the CO₂ experiments. (There were also minor increases in quartz, albite, dolomite and mica, and minor decreases in K-feldspar and kaolinite.) In support of these data, modeling by Gaus et al. (2005) indicated that feldspar alteration is the dominant long-term reaction with CO₂.

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²⁶ Most chemical reaction experiments were performed with pulverized samples with only a few tests using rock fragments. Contrary to expectations, Kohler et al. observed that fragment experiments displayed significantly more reactivity than the experiments involving powders.

²⁷ Except for Fe.

²⁸ No sampling was conducted during any of the experiments by Alemu et al. The shortest test was 7 days, and therefore, results for earlier times are not available.
2.4.2.4 Temperature Dependence

Limited test data suggest that the reactions of mudstones with CO$_2$ and brine exhibit moderate to little sensitivity to temperature changes. Test results by Alemu et al. (2011) show only minor changes in various concentrations for a temperature change from 80 °C to 150 °C. At 200 °C, only moderate concentration changes are evidenced in K, Ca, SiO$_2$, Mg and Fe, with a significant variation in only Al. Most concentrations also decreased with increasing temperature except the concentration of K.

Relatively small changes were also noted by Credoiz et al. (2009) with two mudstones over the range of 80 °C to 150 °C with exposure to CO$_2$ and brine. Concentrations of Ca, K, Mg, and Na increased moderately with increased temperature, and the Si concentrations remained stable. The authors also noted that the Fe concentrations in all the experiments were difficult to interpret.

Based on a review of the field, Liu et al. (2012) concluded that shale is geochemically reactive to CO$_2$ exposure at higher temperatures for geosequestration (150 °C to 200 °C), but relatively inactive at the lower end of the range (50 °C to 80 °C). However, this conclusion may be too expansive as both Alemu et al. (2011) and Credoiz et al. (2009) observed that at lower temperatures, the pH of the CO$_2$ solution is higher due to the increased solubility of CO$_2$ in brine.
with decreasing temperature. This increased acidity, in turn, enhances the release of SiO₂ and Fe into solution. Therefore, the reactivity of CO₂ at lower temperatures may be significant as well.

### 2.4.2.5 Porosity and Structural Changes

CO₂ can react with shales and mudstones to alter the rock’s microfabric and change the connected porosity of the rock. These changes are dependent on mineralogy and on the specific ambient conditions. Note also that alteration of a sample, while related to porosity changes, may not always cause increased porosity in the matrix, and porosity changes may also occur in unaltered portions of a sample due to particle transport.

The change in porosity of mudstones varies with mineral composition and the alteration process can affect only a specific range of the pore sizes. Data from Wdowin et al. (2013) indicated that shale exposure to CO₂ with brine changed the pore size distribution of one of two mudstones, with one mudstone sample showing increases in the pore size distribution over the range of 2 ηm to 15 ηm after 20 months of exposure at about 25 °C and 6 MPa. The alteration processes created a new peak in the distribution at 4 ηm, and new pores in the range of 2 ηm to 4 ηm in size. However, testing with a second rock type (a claystone) showed little change in porosity under the same conditions. It was mentioned by the authors that the second rock material had a lesser clay mineral content, suggesting that the observed CO₂ reactions were mineral-content-dependent.

Changes can affect the range of connected and total porosity. Testing by Mouzakis et al. (2016) examined the changes in both the connected and the isolated porosity of two different mudstones after exposure to 1) brine-alone and 2) brine with scCO₂. The tests were performed at 160 °C and 15 MPa for a duration of approximately 45 days. For tests with brine and scCO₂ and comparing these results to the brine-only case, the authors observed a decrease in the connected porosity but an increase in the isolated porosity for both rock types. The associated changes to overall porosity, however, were small, as the total porosity of one rock type increased moderately (19%) and the total porosity in the other decreased marginally (2%). Differences in porosity distributions between the brine-only and the CO₂-brine samples in one rock type was attributed to the range of pore sizes of roughly 1 ηm to less than 300 ηm in diameter, while in the other rock type, the pore size change was more in the range 1 ηm to roughly 150 ηm.

Along similar lines, Garrido et al. (2013) observed an increase in pore sizes in the range of between 0.7 ηm and 7.0 ηm in comparing pore size distributions from before and after testing. These experiments involved CO₂-water-rock reactions conducted for 60 days at conditions of 8.4 MPa and 53 °C. The post-test pore size distribution also showed a new peak about 2.5 ηm with an overall shift to smaller sizes of the pore size distribution (less than 10 ηm) and with very minor increases in porosity at pore sizes of 50 to 100 ηm.

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29 The sample with a smaller amount of carbonate showed a larger decrease in connected porosity, and a moderate increase in total porosity.
There are also short duration results reported by Jiang et al. (2016) for interactions of mudstone with scCO₂ alone. Tests were generally conducted at 40 °C and 8 MPa over a range of exposure durations up to 5 days. The total porosity data were highly variable with test duration, but suggest a small increase in porosity with scCO₂ exposure duration. However, total porosity shows no consistent relationship with test temperature after an exposure of 4 days (over a range of 40 °C to 90 °C). In other investigations, Lahann et al. (2013) found little change in pore size at 150 °C between tests of brine with CO₂ and without CO₂ exposed for time periods up to 42 days.

Testing by Yin et al. (2016) exhibited various changes in mudstone porosity with scCO₂-only exposure. From tests with a duration of 30 days, and conducted at 40 °C and 16 MPa, the porosity data indicated exposure to scCO₂ induced only a small reduction in the total pore volume for four rock samples together with the dissolution of some organic content. However, the changes were not uniform across the distribution of pore sizes. While there was little change in volume of the mesopore size pores for all samples, there was a significant decrease in the micropore volume in all samples together with a variable effect in the macropore volume (with both large increases and decreases). The authors also noted that there was a decrease in the fractal dimension of the pore structure in these tests, suggesting a decrease in the roughness of connected porosity. They also concluded that as scCO₂ dissolved a portion of the organic matter in a shale, the number of micro- and mesopores decreased, thereby decreasing the adsorption capacity of the overall sample.

In summary, exposure to CO₂ (and brine) in many cases can induce significant alteration and changes in the amounts of connected and isolated porosity of a mudstone. However, these changes are not uniform across the range of pore sizes, will vary with mineral composition, and may only induce minor changes in the total porosity of a sample. In general, pore volumes near the pore size of 1 n and 4 n showed the most change in tests. From scanning results, the pore size of generated secondary porosity appears related to the size of the mineral inclusions in the mudstone matrix itself, indicative of plucking. And finally, changes in the pore network can also occur due to the chemical reaction of mudstones to anhydrous CO₂ (or CO₂ with only minor amounts of H₂O) in some cases, but appears to be much less reactive than with H₂O.

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30 The presence of water is not known from the paper description. Sample preparation was not described in the report, and it is unclear if samples were dried prior to tests or tested with some water content.

31 The presence of water is not known from the paper description. The authors did not describe if the samples had an appreciable water content, had been dried and did not indicate the use of any fluid in the reactor. They also did not indicate if the scCO₂ was dry.

32 In this context, mesopores are defined with a diameter of less than 50 n, but greater than 2 n, macropores are defined as having diameter greater than 50 n, micropores are defined as having a diameter less than 2 n (Rouquerol et al., 1994).
2.4.3 Observations

Examining the available literature, the following are observations on various aspects on the chemical effects of CO₂:

- Exposure of mudstones to CO₂ will induce reactions dominated by carbonic acid, particularly in reacting with minerals like dolomite and calcite. These reactions will be dependent on the mineralogy of the mudstone as well as the chemical composition of the ambient fluid (brine).

- Reactions to CO₂ with mudstone (including the dissolution of clay minerals and precipitation of secondary clay minerals) have been observed over a wide range of temperatures (from room temperature to 250 °C).

- The mixture of CO₂ with brine is more reactive to mudstone than CO₂ alone in causing alteration, dissolution, and precipitation. Exposure to CO₂ alone (dry CO₂) has a reduced effect on apparent mudstone response.

- Reactions in the lab occur rapidly with the introduction of CO₂ and most mineralogical/ion changes become stable after several days. However, some long-term reactions have been observed up to 5 years after the start of testing.

- The temperature-dependence of the reactions of mudstones to CO₂ and brine exposure appears to be minor.

- Many chemical tests have been performed at elevated temperatures (150 °C to 250 °C) to accelerate chemical processes and increase the extent of alteration, but are not entirely representative of expected in situ conditions, especially as the alteration of clay minerals, as well as pH, is expected to be temperature dependent.

- Porosity changes due to CO₂ exposure are variable across the distribution of pore sizes. Interactions can decrease connected porosity, increase isolated porosity and appear to affect smaller pore sizes more. The total porosity shows little change in testing, however. Decreasing connected porosity can potentially reduce permeability, but reactions can also reduce flow path roughness, which in turn, can increase permeability.

- Testing to date of geochemical reactivity of CO₂ has focused on CO₂ dissolved in H₂O, and no data on the effects of H₂O dissolved in CO₂ (wet CO₂) have been systematically studied.

- As mentioned for sorption testing, most chemical tests are performed on pulverized/ground samples. The grinding process destroys the microfabric of the samples, and does not readily allow for the extrapolation of laboratory data to field predictions.

33 Note that permeability may not be fully dependent on the amount of connected porosity, as main flow paths can be enhanced during the process with a net increase in effective permeability (despite many connected pores become isolated).
• No mention of the influence of microbial content on these chemical reactions was noted (if present).

In review of the current experimental literature (including reviews such as Gaus, 2010), the following recommendations are made on geochemical investigations:

• Studies should focus on intact shale samples (rather than clay minerals) to define the response to CO₂.  

• Testing should focus on identification of the clay minerals and the mineralogy of the mudstones samples directly used in testing.

• Efforts should include fully-identifying “typical” initial chemical conditions for analyses (as geochemical reactions are a direct function of the initial in situ chemical conditions).

• More definition is required of the thermodynamic properties of relevant mineral phases that precipitate due to CO₂-rock interactions.

• The impact of potential temperature differences between the injected CO₂ and the reservoir rock on geochemical interactions should be examined.

• Additional study of the kinetics of long-term reactions should be conducted to reduce uncertainty in assessing mineral trapping capacity.

• Long-term reaction paths should be investigated further, especially with respect to the existence of intermediate mineral phases. Note that little data is available on extended geochemical reactions with CO₂, with most testing chemical immersion experiments conducted over periods on the order of days with few exceptions (e.g., testing by Bateman et al., 2013).

2.5 EFFECTS OF CO₂ ON MECHANICAL RESPONSE

2.5.1 Observed Changes in Strength and Modulus

2.5.1.1 General

As discussed, CO₂ exposure can alter the mudstone microfabric, which in turn can be expected to affect the mechanical response of the rock. Limited investigations using mechanical tests have examined the effect of short-term exposure CO₂ on various rock properties. In general, the measured effects have been moderate to negligible. This testing has included indirect tension tests, point load tests, and uniaxial compression strength (UCS) tests. Modulus and Poisson’s ratio determinations together with acoustic wave (P-wave, S-wave) monitoring were also performed during the UCS testing. A description of the test results is provided in the following sections, followed by an evaluation of the data.

34 Tests should be performed on shales with a range of characteristics. Characteristics include the mineral content of the rock unit, including the amount and type of clay minerals present, strength and organic content.
2.5.1.2 Indirect Tensile Strength Results

Ojala (2011) performed indirect (Brazilian) tensile testing of Pierre Shale samples. Prior to testing, the samples were brine-CO₂-aged for 7 days. Control samples were exposed to a brine-only solution for 7 days as well. The tensile tests were conducted at room temperature and pressure. The brine-only samples had an average tensile strength of 0.70 MPa, ranging roughly from about 0.58 to 0.88 MPa. The CO₂-brine aged samples had a slightly lower average tensile strength of 0.65 MPa, with results ranging roughly from about 0.54 to 0.72 MPa. Numerically, this is an average decrease of approximately 7% after 7 days. However, the author concluded that the small difference in average UCS strength reflected natural variability of the rock, and hence stated that there was no significant effect of CO₂ exposure. The Brazilian (splitting) indirect tensile test used by Ojala (2011) is illustrated in Figure 8.

![Illustration of Brazilian (indirect) tensile test with elliptical platens.](image)

2.5.1.3 Point-Load Testing Results

A set of point load index tests was performed on Pierre Shale by Zhou et al. (2010) after exposure of the samples to a CO₂ gas atmosphere. Tests were conducted at room temperature

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35 The samples were placed in a CO₂-saturated brine at 80 °C to 100 °C and at a pressure of 25 MPa; the brine was saturated salt water (3.5% NaCl).

36 Prior to testing, the samples were stored in a container of CO₂ gas at atmospheric pressure for about 90 days (3 months). Control samples were stored in air, and no description of moisture control was provided.
and pressure. In comparison to samples stored only in air, the CO2-exposed samples showed a decrease in average point load index value from 6.4 MPa to 5.7 MPa, or about a decrease of 11%. Translating these values into UCS strengths using the approach by Zhou et al. (2010) yields estimated UCS strengths averaging 36.1 MPa and 38.3 MPa and for the CO2-exposed and the air-only samples, respectively, showing a 6% decrease in UCS strength.

2.5.1.4 Uniaxial Compression Strength Results

UCS tests were performed on shale and sandstone by Choi and Song (2012). These samples were first gas-aged under varying environments for 14 days and then dried prior to testing. The differing environments included a) brine-only, b) brine and aqueous CO2, and c) brine and scCO2. The brine-only sample had a UCS strength of 121.9 MPa. The UCS strength for the aqueous CO2 and scCO2 conditions were 145.5 MPa and 111.8 MPa respectively. Therefore, testing with the aqueous CO2 resulted in a small strength increase (19%), while testing with scCO2 exhibited a small strength decrease (8%) in comparison to the brine-only case. (However, the authors concluded that shale specimens reacted with H2O-scCO2 and subjected to an applied load more than 60% of the unreacted peak stress will fail due to the continued growth of unstable cracks at longer times.)

UCS testing by Lyu et al. (2016b) on Longmaxi Shale from China exhibited moderate effects after CO2-gas aging. Samples, which had a high natural water content (15%), were aged over periods of 10 and 20 days, slowly depressurized and tested at 40 °C and at ambient pressure. Results for samples aged for 10 days exhibited an average UCS value of 219.9 MPa normal to bedding and 68.2 MPa parallel to bedding, compared to unreacted samples with average UCS values of 226.8 MPa and 93.0 MPa normal and parallel to bedding, respectively. This is a 3% decrease in strength normal to the bedding, and 27% decrease parallel to bedding. Increasing the duration of aging to 20 days, the uniaxial strength decreased further to 185.0 MPa and 64.8 MPa normal and parallel to bedding, or for an 18% and 30% decrease from the unreacted strength, respectively.

A second testing program of uniaxial compression testing was reported by Lyu et al. (2016a) with Longmaxi Black Shale. In this program, samples were treated or aged with CO2 and water at two differing pressures: (1) at 7 MPa (labeled, “gaseous”), and (2) at 9 MPa (labeled, “supercritical”). The black shale samples were cored parallel to bedding. Exposure times were extended from the prior program to 10, 20, and 30 days. All treated samples were tested at 40 °C, but the unreacted control samples were tested at room temperature.

37 Computed using a subset of the data from Zhou et al. (2010), with the lowest value from both test groups excluded in computing these averages.
38 Shale samples were placed in a pressure cell at 10 MPa at 80 °C to 100 °C. Conditions included exposure to: (1) water, (2) brine, (3) scCO2, (4) H2O and scCO2, and (5) brine and scCO2. Swell tests were also conducted by these authors (see Section 2.3.4)
39 Uniaxial strengths over 27 MPa for a shale classifies the samples as hard shale (e.g., Lindner, 2016a).
40 Shale was exposed to CO2 gas in a pressure cell at 7 MPa at 40 °C.
Results for the gaseous samples showed that UCS values of 40.42 MPa, 31.36 MPa, and 25.63 MPa for treatment times of 10, 20, and 30 days, respectively. Compared to a corrected unreacted UCS strength of 73.5 MPa, these values represent a decrease of 45%, 57%, and 65% decrease for treatment durations of 10, 20 and 30 days, respectively. Similarly, for the supercritical samples showed average UCS values of 39.02 MPa, 30.72 MPa, and 19.97 MPa for treatment times of 10, 20, and 30 days, respectively. These values are only slightly reduced from the gaseous samples and represent about the same decrease from the corrected UCS control sample for 10, 20, and 30 days of treatment.

Normalized UCS results from Lyu et al. (2016a, 2016b) are shown in Figure 9. Differences in the treatment process and in the shale type used in the two programs make a comparison of the data problematic. However, there is a general trend of decreasing strength with time for both data sets. There also appears to be only a small difference in strength due to the two treatment options (gaseous and supercritical) used by Lyu et al. (2016a). The increased reduction in strength in data is noted by Lyu et al. (2016a) versus Lyu et al. (2016b) is possibly reflective of the softer, black shale rock unit with increased TOC, although both shale types evidence high strengths for a mudstone. The sharper decrease in the black shale samples may also reflect the use of water in the treatments by Lyu et al. (2016b), which potentially increased the reactivity of the treatment process, and therefore further decreased the strength. It can also be suggested that the strength normal to bedding decreases slower with treatment duration than strength parallel to bedding from data by Lyu et al. (2016b).

2.5.1.5 Elastic Parameters and Other Indicators from Uniaxial Testing

Elastic parameters measured by Choi and Song (2012) during the UCS testing showed little to no effect on Young’s Modulus and Poisson’s ratio of the scCO$_2$-brine exposed samples in comparison to the brine-only samples. However, P-wave results on dried samples exposed to scCO$_2$ and brine after testing exhibited a minor effect, showing a reduced velocity of 2.94 km/s in comparison to 3.24 km/s recorded before testing (a 9% decrease). However, the brine-only sample also showed a minor decrease in P-wave velocities over testing as well, decreasing from 3.53 km/s before testing to 3.45 km/s after testing (a 2% decrease).

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41 For the “corrected” value, the unreacted average UCS value of 58.82 MPa at 22 °C for the black shale was increased 25% to 73.5 MPa to compensate for an expected increase in strength at a higher temperature of 40 °C. Note that testing by Lyu et al. (2016b) indicated that average UCS strength increased by 27% with increased temperature from 22 °C to 40 °C, measured parallel to bedding for the untreated samples.
Note:

a Data from Lyu et al. (2016a, 2016b). Samples were tested both normal to and parallel to bedding by Lyu et al. (2016b); samples tested by Lyu et al. (2016a) were all tested parallel to bedding.

b Data from Lyu et al. (2016b) was normalized to an untreated average UCS strength at 40 °C of 226.8 MPa and 93.0 MPa for normal and parallel to bedding respectively.

c Data from Lyu et al. (2016a) was normalized to an untreated average UCS strength of 53.8 MPa at 22 °C (labeled as “Authors’ Values”) and to an adjusted UCS strength, reflective of 40 °C of 73.5 MPa (labeled as “Adjusted” values).

d Lyu et al. (2016b) treated samples with CO2 gas at 7 MPa. Lyu et al. (2016a) treated samples with CO2 and water at a pressure of 7 MPa (gaseous) and at 9 MPa (supercritical).

e Samples were cylindrical, 30 mm in diameter and 60 mm in height for Lyu et al. (2016a) and 38 mm in diameter and 78 mm in height for Lyu et al. (2016b). All treated tests were conducted at 40 °C.

Figure 9: Changes in normalized UCS values with CO2 treatment (reaction) time based on data from Lyu et al. (2016a, 2016b).
Elastic parameters measured by Lyu et al. (2016b) on Longmaxi Shale showed variable results after CO₂ exposure at 40 °C. The moduli decreased after exposure for 10 days to an average Young’s modulus of 9.0 GPa and 8.8 GPa normal and parallel to bedding, in comparison to unreacted samples with average modulus values of 14.2 MPa and 12.7 MPa, respectively. This is a 37% and 31% decrease in stiffness, normal and parallel to bedding. However, with an increased exposure to 20 days, the average Young’s modulus increased from the values at 10 days to 11.0 MPa along both axes, reducing the total change (decrease) to 22.6% and 13.8% normal and parallel to bedding, respectively, in comparison to the unreacted values.

The brittleness index measured during UCS testing by Lyu et al. (2016b) showed minor changes due to CO₂ exposure. Parallel to bedding, the index increased throughout testing, increasing to 63% at 10 days, and then to 70% at 20 days from the unreacted value of 58%. Normal to bedding, the index first decreased slightly then increased with exposure duration, with values of 73% and 75% at 10 and 20 days, respectively, in comparison to a value of 74% for the unreacted case. In addition, acoustic emissions monitoring indicated that the peak cumulative acoustic emission increased with exposure duration and emissions were higher parallel to bedding than normal to bedding.

Elastic parameters measured by Lyu et al. (2016a) on Longmaxi Black Shale exhibited a decrease with reaction time and the modulus values were similar for either aging process (i.e., for both gaseous and supercritical sets). The elastic moduli for gaseous treatment were 3.79 GPa, 2.60 GPa and 2.39 GPa after 10 days, 20 days, and 30 days of treatment, respectively; versus the average elastic moduli for supercritical treatment of 3.64 GPa, 2.47 GPa, and 2.28 GPa after 10 days, 20 days, and 30 days of treatment, respectively. Using an adjusted unreacted modulus value of 6.5 GPa as a basis, the values reflect decreases of 42%, 60%, and 63% for gaseous samples, and 44%, 62%, and 65% for the supercritical samples after 10 days, 20 days, and 30 days of treatment, respectively.

The brittleness index for tests by Lyu et al. (2016a) also decreased for both gaseous and supercritical test groups, with a significant drop at 30 days to a brittleness index of about 50% from an index value of 84% for the unreacted samples. The supercritical test group evidenced a lower brittleness index during the testing, but the difference decreased substantially at an exposure of 30 days.

As for Lyu et al. (2016b), acoustic emissions monitoring by Lyu et al. (2016a) indicated that the peak cumulative acoustic emission increased with exposure duration; they were also higher for the supercritical group than for the gaseous group of samples in Lyu et al. (2016a).

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42 The brittleness index is defined by Lyu et al. (2016b) as the ratio of elastic (recoverable) strain to total strain evidenced in a loading/unloading cycle.

43 The unreacted sample’s average modulus was 5.22 GPa at 22 °C.

44 The unreacted modulus at 22 °C was increased 25% to compensate for an expected increase in modulus at a higher temperature of 40 °C.

45 The peak cumulative A/E energy for the gaseous group and supercritical group samples was 130,137 µJ and 147,862 µJ respectively at 30 days of exposure (Lyu et al., 2016a).
2.5.2 Summary of Observations and Recommendations

From available testing, the mechanical effects of exposure to CO2 and brine, the following observations can be made:

- Strength tests (i.e., UCS, point load, indirect tensile tests) and compressibility measurements (Young’s modulus, Poisson’s ratio) are both affected by exposure to CO2. The effects vary from insignificant to substantial, depending on the duration and type of CO2 exposure/aging. In addition, the projection of the data trends for longer CO2 exposure durations is uncertain but could result in very substantial reductions in strength and moduli with larger exposure durations.

- The presence of H2O in sample treatment apparently accelerates the mechanical reaction of mudstones to CO2. The addition of H2O to the aging of the samples by Lyu et al. (2016a) decreased UCS test results by roughly a factor of 2 in comparison to results by Lyu et al. (2016b), which aged samples without water (Figure 9).

- The extent and type of alteration of the tested samples are unknown. No sectioning of the specimens was described in the literature to evaluate alteration. Given the impermeable nature of mudstones (shales) and the larger sample size used in mechanical testing, penetration extent of the alteration front into the rock matrix is uncertain. Therefore, the effectiveness of the methods of CO2 treatment of the samples can be not evaluated, and no correlation to the amount of alteration can be inferred.

- As a corollary, as the extent of reaction penetration is unknown in available tests, the CO2-penetration and reaction with the rock samples may have been very limited and restricted to the near-surface volume of the cylindrical samples (a skin effect). Alteration can readily proceed with powered samples (typically used in chemical reaction and sorption tests), but given the relatively impermeable nature of mudstone and the larger sample size, the treatment processes may have been insufficient to reach the core center or progress very far at all into the sample volume. Alteration could have been therefore nonhomogeneous across the entire sample volume and may explain the variability in test results.

- The effect of CO2 aging on mechanical properties appears to differ with respect to sample orientation, with an increased effect parallel to bedding in comparison to normal to bedding. This is demonstrated by various indicators, such as the reduced impact in UCS values from samples tested normal to bedding in comparison to those tested parallel to bedding (e.g., Lyu et al., 2016b). In addition, Lyu et al. (2016b) also reported increased acoustic emissions parallel to bedding, indicative of more deformation along this orientation. It is inferred that the difference in response can be related to differences in effective permeability of a mudstone, with increased permeability parallel to bedding leading to more flow and therefore more alteration in this orientation.

- With a nonuniform effect on the sample matrix, the anisotropy of the samples changes with CO2 exposure duration. Sample anisotropy is generally expressed as the ratio of
average strength or modulus values normal to and parallel to bedding. From data reported by Lyu et al. (2016b), Young’s modulus anisotropy ratio of unreacted samples is 1.27 at 22 °C, and 1.12 at 40 °C, demonstrating the anisotropy. However, this ratio becomes 1.0 (i.e., non-anisotropic) after 20 days of CO₂ treatment. In contrast, the UCS strength ratio from Lyu et al. (2016b) increases with CO₂ treatment. The strength ratio of unreacted samples is 2.63 at 22 °C, and 2.44 at 40 °C, while after 20 days of CO₂ treatment, the ratio at 40 °C is increased to 2.85.

- The effect of swell induced by CO₂ on mechanical response could not be evaluated due to lack of data. Unfortunately, swell was not measured during the more extensive programs by Lyu et al. (2016a, 2016b), and lack of data prohibits any correlations of swell behavior with changes in strength or modulus.

Recommendations based on mechanical testing exposed to CO₂ are:

- Cross-sectioning of samples both laterally and axially to determine the extent of alteration and type of alteration should be performed as part of testing. This will address concerns of insufficient aging, nonuniformity of alteration, and allow assessment of how alteration is influenced by bedding.

- Triaxial testing of mudstone samples is needed (and strongly recommended) to provide a more comprehensive understanding of mechanical strength and modulus changes due to CO₂ under realistic in situ conditions. While UCS and point load tests provide some insight into mechanical effects, they are essentially index tests and do not capture the effect of pressure in the data as would occur underground.

- Temperature should also be examined in mechanical response as it also may have a significant impact on the processes, especially considering the effects seen in data from Lyu et al. (2016a).

- To fully understand the effect of CO₂ exposure on the mechanical response, mineralogical determinations are necessary to properly assess the mineral content of the samples before and after testing.

- Water content measurements of samples both prior to and after testing are needed. As H₂O can affect reactivity, it is necessary to evaluate the amount of H₂O available for reactions during testing as well as during aging, and any changes that could occur.

- Deformation measurements are required to be made during and prior to these tests to evaluate the extent of swelling. It can be suggested that increased swell from CO₂ exposure will correlate with a reduction in strength, but this is unsupported by data.

- As part of any test program, samples treated with brine-alone should be tested to provide a consistent basis of comparison for isolating the effect of CO₂. Comparison of CO₂-brine exposed samples to data from unreacted samples does not allow for the separation of the

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46 For example, the International Society for Rock Mechanics defines the “Strength Anisotropy Index” for point load testing as the ratio of mean point load strength values measured perpendicular to planes of weakness to those measured parallel to the planes of weakness (taken here as bedding planes) (see ISRM, 1985).
effect of the testing fluid (brine) from the effects of CO2 with brine, thereby obscuring the
effect of CO2 alone.

- Methods used to treat or age the shale samples with CO2 should be researched to find an
optimal and effective approach for exposing larger samples to CO2.

2.6 EFFECTS OF CO2 ON PERMEABILITY

2.6.1 Background

Prior to describing permeability measurements with CO2 and mudstones, a perspective on the
flow of CO2 and brine in the rock mass is appropriate to fully understand the competing
processes evident in the data. Given the potential chemical reactions discussed earlier, as CO2
moves through a mudstone rock mass, either by matrix or fractures flow, it will alter the macro-
and microfabric to some extent, depending on the fluid and mineral composition. This results in
a dynamic process in the subsurface, with an overall process that is both location-dependent and
time-dependent.

The alteration process is initiated by the acidic fluid (carbonic acid) induced by injecting CO2 in
the subsurface. The acid will (after a short period of time) alter and weaken the rock, allowing
the flow to erode or pluck the adjacent material, and particulates to enter the flow stream. The
alteration effect will diffuse into the adjacent rock as a front or series of fronts based on specific
alteration processes. Along the fracture itself, however, the fluid is buffered with continued
distance along the flow path, reducing pH and allowing for precipitation of secondary minerals.
The particulates and secondary deposits will tend to close pores or apertures restricting the flow
path especially along alternative flow paths where flow velocities are low. The secondary
minerals deposits may also inhibit reactions of the material underneath them as well.

Examining fracture flow, these dynamic flow conditions are illustrated in Figure 10. The overall
flow will reflect mechanical-hydrological-chemical coupling, as for example, changes in
pressure will affect the apertures controlling flow, perhaps closing and reducing flow velocities,
and the flow velocities, in turn, will affect the rates of chemical reactions. The alteration process
at the fracture surface will diffuse into the adjacent rock matrix at a rate depending on the
composition of the fluid flow and rock mineralogy and microfabric.

This will induce increased porosity and precipitation near the fracture, but this effect will
decrease with flow distance as the fluid becomes buffered. Deposition will also occur further
along the flow path and the secondary minerals will close parts of the fracture system. Further,
included in this process (but not shown) is the effect of the combined flow of CO2 and brine in
the fracture, i.e., a two-phase flow system with brine as the wetting fluid. The process may be
impacted by fracture infillings such as calcite, which can also react with the CO2-brine mixture.

The competing processes along the flow path make the overall effects of CO2 on the mudstone
time-dependent as well as path-length-dependent. This increases the difficulty in replicating in
situ conditions in the laboratory as for example, requiring a longer path-length to study the
deposition than can be readily implemented in a small-scale laboratory experiment.
There may be several different alteration fronts within the shale. See also MacQuarrie and Mayer (2005) for extensive discussion related to nuclear waste.

**Figure 10:** Illustration of some mechanisms involved in fracture flow with CO$_2$. 
2.6.2 Gas Permeability Tests with CO₂ on Intact Samples

Due to the low permeability of mudstones, permeability determinations with CO₂ gas have been performed using both steady-state and transient (e.g., pulse-decay) methods. In many cases, the response of CO₂ gas (a sorbing gas) is compared to the response of non-sorbing gas such as He. Results are summarized in this section based on a selected number of gas permeability measurements described in more detail in Appendix D.2.1.

As noted by several authors, CO₂ gas in mudstone has a lower permeability than He gas (e.g., Miller et al., 1980; Al Ismail et al., 2014; Guo, 2014). The CO₂ permeability of intact mudstone also has been observed to decrease (or stay essentially constant) with increased pore (gas) pressure in testing. In contrast, He permeability increases with increased pore pressure (Elsworth et al., 2012; Guo, 2014). In addition, CO₂ permeability also decreases with increased sample density as evident in tests by Kumar (2014). However, data indicates there is little effect of simple effective stress on mudstone permeability with CO₂ as observed by Al Ismail et al. (2014).

As may be expected, exposure to CO₂ appears to decrease the total gas permeability of intact mudstones with increasing exposure time. As observed by Miller et al. (1980), He permeability measurement made before and after CO₂ exposure showed a significant effect of CO₂ treatment. For a test with a short duration (25 minutes) of CO₂ treatment (CO₂: 33%, 4.6 MPa, 17° C), the He permeability decreased by 75% after CO₂ exposure from that before CO₂ exposure. It was also observed that this decrease could be reversed with He flow through the sample, and the permeability was restored to almost the initial permeability value after 140 hours of He flow. A longer duration test of 25 hours was also observed to have little effect on flow. However, continued, longer treatments with CO₂ by Miller et al. induced a more substantial decrease in permeability. One sample exhibited a decrease in He gas permeability of about two orders of magnitude after 64 hours of treatment (CO₂: 33%, 4.1 to 4.6 MPa). This effect showed only a minor reversal/increase with subsequent flow of He gas.

Elsworth et al. (2012) showed similar results with two tests using both He and CO₂ gas alone. Samples were first tested with He gas, then permeabilities were measured with CO₂ gas, and then again retested with He (i.e., reswept). The total permeability of both samples showed approximately a 10% decrease in the final He measurement from the initial He measurement.

47 It has been suggested that the decrease in permeability is an effect of swell closing pore space and microfractures in shales (e.g., Kumar et al., 2016).
48 A simple effective stress is defined by the authors as the confining pressure minus the pore/gas pressure.
49 Submergence in a H₂O and CO₂ solution, at a specified temperature and pressure conditions.
50 The duration of the CO₂ flow was not stated.
However, other evidence has shown an increase in permeability with CO\textsubscript{2} flow. Gas breakthrough tests\textsuperscript{51} by Wollenweber et al. (2009) showed that repetitive testing with CO\textsubscript{2} reduced the entry pressure by 33\% and increased the permeability of a marlstone sample from 1.0 \( \eta \)D to 2.9 \( \eta \)D. Also, a slight increase in permeability coefficients was detected after a CO\textsubscript{2} breakthrough by Amann-Hildenbrand et al. (2013).\textsuperscript{52}

The effect of CO\textsubscript{2} on mudstone is also influenced by the sample fabric/anisotropy as demonstrated by data from Al Ismail et al. (2014). Measurements with both He and CO\textsubscript{2} showed higher permeabilities parallel to bedding versus normal to bedding by 2 to 3 orders of magnitude. However, CO\textsubscript{2} flow evidenced a lower permeability anisotropy ratio\textsuperscript{53} than with He; the He anisotropy permeability ratio was 10\textsuperscript{-2}, while the CO\textsubscript{2} anisotropy ratio was approximately 10\textsuperscript{-3}. Conceptually, the introduction of CO\textsubscript{2} gas into the sample altered the permeability (from the initial He permeability) for both orientations but to differing degrees. The He permeability normal to bedding (i.e., the vertical sample), decreased from 14 \( \eta \)D before CO\textsubscript{2} testing to 6 \( \eta \)D after CO\textsubscript{2} testing, at a simple effective stress of 6.9 MPa. In comparison, the horizontal sample (parallel to bedding) showed an increase (sic) from 1.4 \( \mu \)D to 2.2 \( \mu \)D. In addition, the hysteresis in the initial He permeability measurements evident in loading/unloading the effective stress normal to bedding was absent in subsequent CO\textsubscript{2} permeability tests and was also not apparent with He permeability testing after CO\textsubscript{2} exposure.\textsuperscript{54}

As described in prior sections, the samples exposed to CO\textsubscript{2} showed several mineralogical effects. The high-carbonate-content marl sample from Wollenweber showed a significant decrease in anorthite, kaolinite, and smectite together with an increase in calcite after breakthrough tests. Analysis of the water-CO\textsubscript{2} solution used by Miller et al. (1980) after treatment of the shale showed increased concentrations of Ca and other alkaline earth and iron compounds.

\textbf{2.6.3 Fluid Permeability Experiments on Intact Samples using CO\textsubscript{2}}

The effects of fluid (liquid) flow through mudstones with CO\textsubscript{2} provide a somewhat different aspect of the mudstone response than with gas. Unfortunately, references on fluid flow with CO\textsubscript{2} have proved scarce in the literature. However, some insight of the effects of CO\textsubscript{2} on fluid flow in intact samples is provided from breakthrough tests conducted with CO\textsubscript{2} by Soldal (2008), Larsen (2011), Skurtveit et al. (2012), and Liu (2013). There are also tests results on reconstituted samples as reported by Olabode (2012) and Olabode and Radonjic (2017a, 2017b). Both sets of references are discussed in more detail in Appendix D.2.2.

\textsuperscript{51} In this context, a capillary breakthrough test is a determination of the required differential pressure of a non-wetting fluid (CO\textsubscript{2} or scCO\textsubscript{2}) to percolate through a sample saturated with a wetting fluid (brine or H\textsubscript{2}O) and reach the lower pressure outlet on the sample, or breakthrough (e.g., see Hildenbrand et al., 2002).

\textsuperscript{52} The authors observed in breakthrough experiments only a limited amount of the rock is exposed to CO\textsubscript{2}.

\textsuperscript{53} The permeability anisotropy ratio is defined as the permeability normal to bedding (vertical) to the permeability parallel to bedding (horizontal).

\textsuperscript{54} No hysteresis was evident in the initial He parallel to bedding. Minor hysteresis was evident with both CO\textsubscript{2} and He in subsequent testing parallel to bedding.
The flow of liquid CO2-brine apparently has an irregular effect on pore sizes. As observed by Soldal (2008), small pore sizes (less than 10 nm) decreased after scCO2 exposure while larger pores (greater than 100 nm) evidenced little change. In contrast, data from Olabode (2012) with restored samples showed a substantial increase in cumulative pore volumes at a pore diameter less than 3.5 nm, but with a decrease in pore volume in the range of 5 nm to 10 nm pore diameters. At larger diameters (10 nm to 200 nm), the data from Olabode indicated an increased cumulative pore volume again. In addition, radial expansion of the sample was primarily at the inflow end of the sample, where the opening of microfractures was evident.

CO2 flow can also alter flow paths and effective permeability. CO2 breakthrough testing from Soldal (2008) indicated that CO2 movement through the rock sample is focused on preferred pathways under the two-phase flow. His results showed that the output stream at breakthrough was comprised primarily of CO2 while the sample itself retained a large amount of water. The flow can also affect the mudstone fabric as compressional wave velocities decreased after the introduction CO2, suggesting a correlation with alteration as described by Skurtveit et al. (2012). Further, a single-phase permeability experiment by Amann-Hildenbrand et al. (2013) showed that CO2-saturated brine induced a small increase in permeability. In their testing, the brine permeability (conducted before and after testing with CO2-saturated brine) increased from 0.20 nD to 0.81 nD after 75 days of flow with CO2-saturated brine.

CO2 flow is also directly related to mechanical response. Skurtveit et al. (2012) concluded that there was a functional dependency between the effective permeability and sample deformation as observed in CO2 breakthrough tests. Their data showed that breakthrough coincided with measured sample dilation. Also from this testing, authors observed that the CO2 breakthrough results from their testing were effectively related to confining stress and effective stress55 and that a breakthrough could not be achieved at higher confining stresses.

Chemical reactivity was again noted in this testing. Consistent with chemical alteration and dissolution described earlier, testing by Berthe et al. (2011) noted increases in Ca and Mg in the CO2 fluid. However, Amann-Hildenbrand et al. (2013) did not observe any significant change in mineralogy in their testing. However, Olabode (2012) and Olabode and Radonjic (2017a, 2017b) in testing with reconstituted samples noted various chemical changes during their testing. Specifically, Olabode and Radonjic (2017b) observed the buffering of pH of the fluid by the sample, together with decreases in anhydrite and dolomite and an increase in quartz in all samples. Data from Olabode and Radonjic (2017b) also indicated varying changes56 in total clay content, as well as changes in chlorite, kaolinite, and illite across the four mudstone samples tested. Estimates of permeability indicated that there was a rapid decrease in permeability on the first day of tests by Olabode and Radonjic, but then the rate changes and permeability decreased only slowly thereafter. Olabode (2012) showed similar but variable changes with three samples and concluded that the response of the samples to the CO2-brine was controlled by minute geochemical changes that were hard to detect.

55 In contrast, Liu (2013) found that the fluid permeability of a mudstone with CO2 showed little correlation with minor changes in confining stress after consolidated to a higher pressure.

56 Some samples showed an increase, while others showed a decrease.
2.6.4 Fracture Permeability Experiments with CO₂

2.6.4.1 General

There are only a limited number of references on fracture permeability tests with CO₂ in the literature, and available experimental programs are described in more detail in Appendix D.2.4. In some cases, recent technology has allowed the evaluation of the fracture surface as part of the testing process with X-ray computed tomography (CT) (e.g., Crandall and Bromhal, 2014; Carey et al., 2015, Moore et al., 2017). This testing permits a more accurate assessment of the fracture aperture and how it changes during testing. However, due to current limitations in equipment scan durations, it is not possible to capture rapid transient fracture response at high resolutions.

Prior to discussing data from permeability experiments with fractures, limitations of this testing should be noted. To study the effect of CO₂ on fracture permeability, it is an obvious necessity to have a sample with a central fracture. In most laboratory efforts, the fracture is aligned along the core axis to achieve a longer path length but this introduces issues in test conditions. In cases where a natural fracture can be found within the core, the fracture is seldom uniformly parallel to the core axis, may be nonuniform in characteristics, may be coated or filled, and is sensitive to sample disturbance. Generating an artificial fracture in a core can be performed by sawing the core axially or by inducing a tensile fracture, but both practices introduce other issues. For example with tensile fracturing, the creation process opens the fracture and induces the loss of some surface material. This makes re-mating of the sample problematic, and introduces nonuniformity between the fracture surfaces. Sawing introduces concerns of nonuniform preferential roughness57 and limits studies to relatively simple, planar fractures. In all three cases, the application of confining stress to the fractured core will induce nonuniform stresses across the fracture especially at the fracture edge along the core surface.

2.6.4.2 Flow Results

Fluid flow through artificial fractures in mudstones show that CO₂ gas permeability is less than He gas permeability at low pressures of 1 to 2 MPa (Kumar, 2014). The permeability for both gases increases with increasing gas pressure, but at significantly different rates. CO₂ gas permeability was observed to increase more rapidly with gas pressure than He, increasing in permeability by about 250% over a pressure range of 1.5 MPa to 4.5 MPa, with the CO₂ gas permeability eventually becoming equal to He gas permeability at about 4 MPa (Kumar, 2014). Conversely, external (confining) pressure will impact flow with some tests exhibiting little to no flow at high confining stresses (e.g., Edlmann et al., 2013).

In addition, fracture fillings can also impact fracture flow. In one case with a filled calcite fracture, permeability results indicated that the mineralization infilling did not fully impede flow due to the larger permeabilities measured (Alnoaimi and Kovscek, 2013). In this case, the gas permeabilities of CH₄, He, and CO₂ all decreased with increasing pore pressure over a pressure range of 0.7 to 4.5 MPa. While the CH₄ and He gas permeabilities were initially higher and close

57 The sawing action can create a concave pattern of roughness across the core surface.
in trend, the CO₂ permeability gas was significantly less at low pressure but changed less with increasing pressure and was approximately equal to the other gases at higher pressures.\(^{58}\)

As for previous testing, the alteration processes involved in fracture flow with CO₂ vary with exposure duration and with sample mineralogy. Short-term tests have typically indicated little to no change in permeability during testing. Tests by Alnoaimi and Kovscek (2013) indicated no apparent short-term effects in their standard permeability tests. Li (2016) indicated that the short duration of gas exposure (from tests over a period of 20 to 22 hours) did not have a significant influence on permeability for both adsorptive or non-adsorptive gases. Edlmann et al. (2013) observed only minor alteration, but their tests did not involve significant volumes of scCO₂ flow (due difficulties in testing). Finally, Crandall and Bromhal (2014) saw no conclusive changes in the fracture aperture on the CT images for two of the three types of shales with durations of 19 to 22 days.

However, data from Crandall and Bromhal (2014) did observe a decrease in permeability with Tuscaloosa Claystone over a period of 39 days at room temperature, as evidenced by a pressure increase from 23 kPa to 30 kPa at a constant injection rate over 30 days. A series of successive tests performed by van Noort and Yarushina (2016a) on the same sample with CO₂ gas showed variable results. Three tests were performed in the series with the second test showing an increase in permeability from the first test but the third test showing a decrease in permeability, with the third permeability value comparable to the first test.\(^{59}\)

At more extreme conditions, Smith et al. (2013) saw substantial evidence of alteration in their testing of a greywacke\(^{60}\) at 200 °C at a confining pressure of 25 MPa. Both dissolution and secondary mineral precipitation were evident at the end of the test. This testing involved a core-flood test which was initially saturated with a simple brine solution. The sample was then subjected to flows of a CO₂-saturated brine for 49 days. The sample evidenced a substantial increase in permeability, with a sharp decline in injection pressure to 4% of the starting value with a constant flow volume.\(^{61}\) They also saw the development of a predominant throughgoing channel along the fracture, which was isolated from other pre-existing larger voids along the fracture. Away from this dissolution channel, larger fracture apertures appeared to have decreased, indicating mineral precipitation. There was also a sharp increase in the concentration of Mg, Ca, Fe, Ba, Sr and Mn in the permeant with the introduction of CO₂, but the concentrations rapidly decreased to an equilibrium value with time (reached after approximately 21 days).

Andreani et al. (2008) saw an increase in CO₂-brine permeability over a period of 33 days with the equivalent fracture aperture for the sample increasing from 4.7 \(\times\) 10\(^{-4}\) m to 6.0 \(\times\) 10\(^{-4}\) m. This testing (at 25 °C) involved cycles of alternating flows of CO₂-brine and CO₂-gas through an

\(^{58}\) The CO₂ permeability was approximately 50% of the He permeability at 0.7 MPa, based on curve fit results.

\(^{59}\) Permeability values were 0.16 \(\mu\)D, 0.32 \(\mu\)D and 0.14 \(\mu\)D for tests #1, test #2 and test #3, respectively. Variation in these results may have also been due to replacement of the sample jacket, re-pressurization, sample compaction and potentially by water leaking into the sample as noted by the authors.

\(^{60}\) Also, termed an argillaceous sandstone.

\(^{61}\) A substantial decrease was seen during the first 14 days of test with brine-alone.
artificial fracture in claystone. Most of the increase in the equivalent aperture occurred as a sharp change evident at the start of each cycle of testing with CO2-brine (following a cycle of testing with CO2-gas). The authors correlated the change in aperture to the duration of the prior flow of CO2-brine. The authors concluded that the alteration occurred during the flow of CO2-brine flow but the altered rock was constrained by the cohesion of clay minerals, so there was no evident change in aperture. However, with the exposure to CO2 gas, the strength of the altered rock decreased (with a loss in cohesion), and the altered material was then swept aside by the subsequent cycle of CO2-brine flow, increasing the aperture at the start of the next fluid flow cycle.

2.6.4.3 Propped Fractures

To examine aspects of hydraulic fracturing, some fracture permeability tests with CO2 have involved fractures coated with natural proppants (sand) and artificial (ceramic) proppants. While these results show no significant alteration, the permeability data trends in these tests with CO2 differ from the results with He gas. Testing of propped fractures (with a single layer or monolayer coating) with CO2 gas has shown a significant decrease in permeability with increasing gas pressure (Kumar, 2014; Li, 2016). Data from Kumar showed a decrease of about 50% in permeability over a gas pressure increase from 1.5 to 4.8 MPa. Li also showed a reduction in permeability of about an order of magnitude in permeability over a gas pressure change from 2 to 8 MPa. However, CO2 permeability data from Li (2016) showed an abrupt halt in this trend at higher gas pressures with a propped fracture; results exhibited little change in permeability over a range of gas pressures of 8 MPa to 11 MPa.

In contrast, He gas permeability with a propped fracture exhibited a general increase with gas pressure with a 15% increase over a gas pressure change from 1 to 6 MPa (Kumar, 2014) or about a 20% increase over a gas pressure range of 2 to 12 MPa (Li, 2016). However, this trend was singular and diverged from permeability tests with other gases. Permeability tests using N2 gas and CH4 gas exhibited a decreasing trend with increasing gas pressure for a monolayer propped-fracture, similar to CO2 (Li, 2016). As these other gases are also sorbed by mudstones, this suggests that sorption influences the trend with gas pressure.

The addition of more proppant seems to have only a minor effect on CO2 permeability. Results from a single-layer propped-fracture and a multi-layer propped-fracture with CO2 gas show little difference in permeability values or in the overall trend with increasing gas pressure. Comparison of data from a test with a 1-layer coating of ceramic proppant with a test with a 4-layer coating from Li et al. (2016) showed only a slightly higher permeability (about 10%) for the 4-layer configuration in comparison to the monolayer results. Also for this testing, the measured surface roughness of the monolayer propped-fracture sample was higher than the roughness of the 4-layer propped fracture or of the clean fracture samples.

2.6.5 Other Related Flow Testing

There is supporting experimental evidence on permeability in the literature from testing that would not (in technical terms) be considered a standard permeability test. For example, Zhou et al. (2016) conducted three hydraulic fracture tests with scCO2 on smaller shale core (100 mm in diameter and 200 mm in height). Two samples of the resulting fractured core were then used in subsequent gas permeability tests with He, N2 and CO2 in the second phase of the test program.
The effective stress was applied in a different manner in these two test phases. Data from this effort indicated that with the all three gases, permeability decreased with increasing effective stress over an effective stress range of about 2.5 to 10.5 MPa. CO₂ permeability decreased about 45% over this range, while CH₄ and He permeabilities decreased about 20% and 10% respectively. The He permeability was higher than CH₄ which in turn was larger than CO₂. The authors also indicated that the permeability values were stress-path dependent with less effect when the effective stress is changed by a pore pressure reduction (first phase) versus changing the effective stress by increasing the confining pressure (second phase).

Supporting evidence of alteration was also collected by Shao et al. (2010). They conducted dissolution kinetics and surface morphology studies on phlogopite core subjected to a chemical batch reactor with a CO₂-saturated brine. Tests were conducted over a period of approximately 6.5 days and at conditions of 95 °C and 10.3 MPa. The authors examined the evolution of alteration across the clay mineral in detail.

Their observations indicated a progression of alteration across the sample surface with time. Initial exposure to the CO₂-saturated brine created dissolution pits across the surface. With continued exposure, these pits became deeper and larger, connecting with other pits and forming channel-like structures as testing progressed. Alteration of the surface continued, but secondary deposits on the surface were formed, inhibiting the dissolution process. The secondary deposits essentially formed islands within the altered area. These islands grew (together with the altered area) but were eventually undermined by the dissolution process and migrated with the flow, collecting elsewhere. In summary, the process evolved in a distinct sequence of events.

2.6.6 Observations

From the foregoing on the effects of exposure to CO₂ and brine on permeability, the following observations can be made:

- CO₂ exposure has a variable effect on the permeability of intact mudstones, and the effect increases with the duration of exposure. The effect also increases with the availability of water or brine (e.g., water-based CO₂ treatment from Miller et al., 1980).
- The effect of CO₂ on the permeability of intact mudstones is influenced by the rock anisotropy.
- The CO₂ gas permeability of intact mudstone samples decreases with increasing pore/gas pressure. Permeability with N₂ and CH₄ gases also decrease with increasing pore/gas pressure but He permeabilities increase with increasing gas pressure.
- Alteration of an intact mudstone due to CO₂ flow is non-uniform with respect to pore size and volume. Alteration will increase the distribution of pore size over one size range but decrease the distribution over another range. As observed in some tests, small pore sizes (less than 10 μm) decreased after scCO₂ exposure, while larger pores (greater than 100 μm) evidenced little change from the same exposure.

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62 A mica (i.e., a phyllosilicates) which is also known as magnesium mica.
- CO\textsubscript{2} fluid flow through intact mudstone is along preferred pathways (connected porosity). These pathways are expected to be the fastest travel paths in the sample fabric but as such may not include all large voids. These preferred pathways can also be expected to experience the largest amount of alteration.

- Sample deformation is related to CO\textsubscript{2} flow in CO\textsubscript{2}-breakout tests, and breakthrough coincided with measured sample dilation. With two-phase flow, CO\textsubscript{2} flow/breakout occurred primarily along selected paths, leaving most of the sample water-saturated.

- The current methods of fracture permeability testing have several limitations in simulating uniform downhole conditions.

- The permeability testing of fractures without a proppant in mudstones exhibited increasing permeability with increasing gas pressure.

- Short-term fracture permeability tests have typically indicated little to no change in permeability with duration during testing with CO\textsubscript{2}. However, in longer-duration fracture permeability tests, both increases and decreases in permeability have occurred, apparently dependent on mineralogy and on the aspects of flow path through the sample.

- Single-layer propped fractures have shown a decrease in gas permeability with CO\textsubscript{2} with increasing gas pressure (as well as N\textsubscript{2} and CH\textsubscript{4}), but He exhibits an increasing permeability with gas pressure.

- Increasing the proppant coating from one layer to four provides only a minor increase in He permeability with the increased coating, but the increased proppant still maintains the same general trend of decreasing permeability with gas pressure.

- At low pressures, the He gas permeability in (clean) fractured rock is typically higher than CH\textsubscript{4} which in turn is higher than CO\textsubscript{2}. However, at increased gas pressures, the permeabilities of these gases in fractured rock become similar.
3. **INFLUENCES OF MODELING ON EXPERIMENTAL EFFORTS**

3.1 **ASPECTS OF CO₂ FLOW**

To provide a context for experimental work, some basic modeling aspects of CO₂ in the subsurface are discussed in this section. Given the foregoing experimental evidence, the accurate modeling of mudstone response is a complex task and needs to address a wide range of possible processes in the subsurface applications.

In considering modeling CO₂ reactions with shale, some cautionary notes on representing mudstones or shales are also appropriate. While often modeled as a single homogeneous unit, mudstones or shales show an inherent variability in the field at both the microfabric and macrofabric scale. This variability is obvious on the small scale in the attempts to classify shale (Lindner, 2016a). Simply, a shale is not a clay (or a clay mineral) and can exhibit a wide range of properties. While appearing homogeneous, the mudstone unit of a single formation can show variability in clay mineral content, in the type of clay minerals present and in other mineral components from one location to another, all which will influence behavior such as swell.

3.2 **FLOW PATH CONSIDERATIONS**

3.2.1 **Example of Idealized Flow Path**

An idealized sequestration case can be used to illustrate some of the potential complexity of the CO₂-dominated flow interacting with a mudstone rock mass. A case can be proposed involving the injection of scCO₂ into a more permeable horizon (reservoir) using a single well, as for example as shown by Rutqvist and Tsang (2002). The reservoir is overlain by a low permeability rock unit (or caprock layer) composed of shale, as shown in Figure 11. Given the injection depth, CO₂ is injected in a supercritical phase.

The overall scenario is relatively straightforward. After the start of injection, the scCO₂ plume flows upward (due to buoyancy) within the reservoir and generally forms a column centered at the injection well. The center of the plume is primarily (dry) CO₂, but as CO₂ mixes with the existing groundwater at the fringes of the plume, there are variable degrees of H₂O-CO₂ saturation within the column. Closer to the plume center, some of the existing groundwater (brine) is dissolved in CO₂ (wet CO₂) whereas, at the outer fringe, CO₂ is dissolved in brine. Initially, buffering the pH of the flow (i.e., from carbonic acid) occurs due to interactions with the rock fabric. Also, CO₂ reacts with other mineral constituents in the reservoir, but these interactions will taper off with the duration of flow.

Upon encountering the base of a lower-permeability caprock during the upward flow, several scenarios are possible, depending on the CO₂ pressure and the extent of fracturing of the caprock (e.g., Bildstein et al., 2010). It is highly likely that, given the lower permeability of the caprock, most of the CO₂ plume will tend to spread out along the reservoir-shale interface with time (e.g., flow in a uniform reservoir with an impermeable caprock is shown in Figure 11).
In addition to potential flow along the well casing-rock interface, some portion of the flow is expected to continue upward into the shale, primarily along the existing fracture system.  

With a caprock with few fractures, most of the CO$_2$ plume will spread radially along the caprock-reservoir interface over a period of years. This flow will also continue to mix with the existing groundwater, further changing the characteristics of the CO$_2$, and changing the CO$_2$ concentration in fractures with location (depicted in Figure 12). Finally, the flow along the interface will continue for large distances (several kilometers) or until a more permeable path is encountered through the shale. Often, this point of increased permeability is visualized as a well or fault.

With the spreading flow, alteration will occur along the shale-caprock-reservoir interface due to matrix flow into the shale. However, this matrix flow and associated alteration will take longer periods of time (estimated in the hundreds to thousands of years for a few meters of progress) due to the low permeability of the intact shale rock fabric. Pressure and saturation of the CO$_2$ front will also decrease with distance from the injection point.

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$^{63}$ CO$_2$ pressure is assumed larger than the respective capillary threshold pressure. It is also assumed that matrix permeability of the caprock is much lower than fracture permeability.
This scenario illustrates a perfectly functioning caprock, i.e., a rock unit that prevents upward flow of CO$_2$. However, this is an idealized case. In reality, vertical fractures can readily occur in sedimentary formations, as well as zones of fracturing. These zones can focus the spreading flow upward as illustrated in Figure 13 (see Wawersik et al., 2001). In addition, a sedimentary rock mass is seldom homogeneous on a large scale, and more-porous rock may be interlayered with the more-impermeable units, providing a faster pathway upwards along a combined stair-step of lateral and vertical connections of these subunits.

Fracture networks in shale will act as the faster path of CO$_2$ through the caprock than diffusion flow. As CO$_2$ moves upwards into the shale, the flow is spatially restricted to fracture network, and so are the attendant CO$_2$-rock interactions. Over the short-term, most CO$_2$ interactions are restricted to the thin zone rock of fracture surfaces along the network of the flow paths through the shale. Diffusion into the matrix may also be restricted by fracture surface coatings or infillings by minerals such as calcite.

Eventually, diffusion processes will extend alteration processes into the adjacent intact rock around the fractures, altering the rock matrix (as a series of alteration fronts moving away from the fracture surfaces). The interactions will be dependent on the mineralogy of the shale (and any infillings), which can enhance flow or impede flow along the fracture system.

64 In more detail, flow will spread laterally until a more permeable zone is encountered, such as a more-fractured or more-permeable zone in the shale, a fault, a well or a borehole. Then, the local fluid flow near the feature will be dominated by upward flow along this more-permeable route. This type of upward flow has been seen in the field (Lindeberg et al., 2000).

65 Note that the dominant flow path can change with time.
3.2.2 Experimental Implications of the Simple Flow Path Case

Examining this simple case, several implications are immediately apparent that can influence studies in the laboratory. First and foremost is the nature of the injected fluid; the injected CO$_2$ will mix to varying degrees with the existing pore fluid. Therefore, in defining test condition, the fluid may span a range of saturation from dry CO$_2$ to wet CO$_2$ then to brine with a range of dissolved CO$_2$.

Secondly, the fluid in the flow is not simply CO$_2$ or CO$_2$ with water, but rather a mixture of CO$_2$ and brine. The brine or groundwater contains concentrations of various salts, minerals, and metals, together with particulates, especially at larger depths. The largest concentration in the solution is NaCl. The two fluids, CO$_2$ and brine, will interact, requiring consideration of two-phase flow. If conditions span different phases of CO$_2$ or include hydrocarbons (such as methane, ethane, propane, etc.), multi-phase flow must be considered in evaluating subsurface flow. As the CO$_2$-brine flow moves upward, the fluid will react with the reservoir rock to some degree, buffering and modifying the fluid, so the brine contacting the caprock will not be a simple saline solution saturated with CO$_2$. The ion concentrations in the fluid and the pH may be highly variable.

In addition, upon contact with the caprock, fracture flow is of the most concern, given the low velocity of diffusive matrix flow. This flow will be along a fracture network, through a more-permeable zone (composed of permeable rock or fractured rock), or along a fault. So studies in the laboratory need to consider fracture permeability and surface effects on the mudstone and the

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66 CO$_2$ with some brine dissolved in it.

67 This discussion excludes manmade features such as wells.
potential for interaction of fluid flow in fracture networks. Fractures may also be coated, adding additional complexity. As noted earlier, precipitation of secondary minerals can also be expected, which may give to concerns of particulate flow that should be addressed in testing to some extent. Further, this creation of secondary minerals and the interactions of the flow with these secondary deposits can obstruct flow and impede dissolution, and thereby need to be also considered in both laboratory testing and in simulations.

Time is another major factor. The flow processes for applications such as geosequestration can involve thousands of years. This requires that laboratory testing on this topic to focus on longer-term experiments; tests performed over a period of hours or a few days may be insufficient for simulating conditions over thousands of years.

### 3.3 PROCESSES AND FACTORS IN CO₂ FLOW

Underlying the experimental results with CO₂ is the interaction of various processes that lead to the observations and data obtained. As shown in Figure 14, there is a complex interaction of processes with CO₂, which control flow through a fractured mudstone.

![Diagram of coupled processes](source.png)

Source: Qiao and Li (2014)

**Figure 14: Illustration of coupled processes in flow from Qiao and Li (2014).**

The processes involved are interdependent and coupled. For example, the mechanical behavior (such as swell) directly affects permeability and flow by closing apertures (hydraulic response), which in turn, can alter chemical reactions (geochemical processes) by limiting fluids to various locations. Thermal processes, primarily temperature, can influence the rate of geochemical reactions, and have an influence on mechanical properties. In addition, there are various cross-connections not shown in the diagram such as the effects of temperature and pressure on salinity and density and on other processes such as swell.
A listing of some of the factors that are necessary to consider in flow modeling of CO₂ in the subsurface is shown in Figure 15. There are various aspects on how to model the fracture network, ranging from factors on characterizing fracture permeability such as aperture and roughness to the type of flow, either laminar or turbulent.

**Figure 15: Selected aspects in modeling CO₂ flow.**

To describe these factors, various property characteristics must be defined, ranging from the surface strength of the rock to the density and viscosity of the fluid. There are also additional influences such as the stress field, the potential for swell and particulate movement. Therefore, in establishing parameters for testing, a range of conditions must be considered, and systematic testing over a possible range of values needs to be addressed.
4. CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

A review of current literature on the interaction of CO2 and mudstones is provided in this report. The review focuses on the interactions that relate to the swell of shales due to the introduction of CO2 into the subsurface. The discussion of these interactions is divided along the following five topics:

1. Sorption of CO2 by clays and mudstones, which can potentially induce swell
2. Observations of the expansive behavior (i.e., swell) due to CO2
3. Chemical reactions of CO2 and brine with shale, which also affect the potential for swell
4. Changes in mechanical properties (e.g., modulus, strength) due to CO2 exposure which may also be related to the extent of swell response
5. Observed effects of CO2 flow on the permeability of intact and fractured rock to examine the effect of swell and other effects on flow

The general approach employed in this review is atypical. Rather than just examining readily available sources and then discussing general topics based on these references, a more time-intensive and detailed approach was employed. After conducting an extensive literature search, the most relevant references on each of these topics were selected for further review. These selected experimental sources were then abstracted to identify the rock units tested, the test conditions, and the basic characteristics of the mudstone that could be pertinent, including TOC, clay content and the type of clay minerals present. For clarity, it was necessary at times to reconstruct figures or develop new ones from the authors’ data. Secondary sources on the material as well as additional explanations on approach and terms used by the authors were added to assist the reader. These abstracts are included in the appendices of the report.

From these abstracts and other literature, trends in the response of mudstone were identified and common observations across the source material were examined. Due to a scarcity of data, it was not always possible to make definitive conclusions, and many of the observations in the report must be considered tentative.

From this review, it is evident that only limited testing data exists on the overall topic and there are large technical subtopics on the interaction of CO2 and mudstone where no data exists. Due to various limitations and constraints in conducting research, authors have focused on specific concerns in their studies so test data is not systematically developed across the field. This restricts the ability to make general conclusions on the topics such as temperature-dependence and the effects of clay content and mineral type on the five topics under review. In addition,

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68 All attempts were made to accurately replicate figures, and modifications were only introduced for accuracy and clarity in presentation.
other factors such as water content, sample disturbance, and the microfabric of mudstones are often not well addressed in the studies, further obscuring the ability to identify data trends. Important conclusions on the interaction of CO₂ and shale from this review are:

*On Sorption:*

- The sorption of CO₂ on mudstones varies with gas pressure and does not follow a typical isotherm (Langmuir) curve. The CO₂ isotherm trend can be divided into three distinct zones/phases as it varies with pressure. In Phase #1, at pressures less than 5 to 7 MPa, the CO₂ excess sorption isotherm increases with increasing gas pressures at a decreasing rate, resembling a Langmuir isotherm curve. Phase #2, the isotherm rate of change increases sharply to a peak at about 10 MPa. (However, this phase is not always evident in test data.) The combined curve of Phase #1 and #2 are like a BET isotherm. However, during Phase # 3, the isotherm decreases sharply at higher pressures (at pressures above 10 to 12 MPa) and can trend to zero.
- The CO₂ excess sorption on mudstones and clays shows an inverse correlation with temperature.
- CO₂ sorption by mudstones is deduced to be a function of the total amount of clay minerals and the type of clay contained in the rock unit. It is also a function of organic content, and correlations have been proposed.
- The CO₂ excess sorption on mudstones varies with water content, but the evidence is contradictory.
- Data were insufficient to identify a direct correlation between sorption and the amount of swell of mudstones. A relationship was proposed by Heller and Zoback (2014) for clay minerals.
- CO₂ excess sorption on mudstones varies with clay mineral type, schematically: 
  
  \[
  \text{Ca-montmorillonite} \gg \text{Na-montmorillonite} \gg \text{illite} \gg \text{kaolinite} \gg \text{chlorite}
  \]
- Interlaboratory comparisons of CO₂ sorption on two types of mudstones showed highly variable results, indicating the need for improvements in current methods and quality standards in measurement procedures.

*On Swell:*

- Mudstones can swell when exposed to CO₂, but the amount of swell is dependent on the clay mineral type(s) and the clay content of the sample.\(^{69}\)
- The amount of swelling strain with clay minerals exposed to CO₂ observed on a lab-scale has been small, generally on the order of less than 1%; swell pressures observed on a lab scale were moderate, ranging from 5 to 11 MPa. However, swell measured at the

\(^{69}\) There can also be swell induced by organic content which is not assessed in this report. Swell due to mineral alteration discussed by Lindner (2016b) may also occur in mudstones.
microscale with clay minerals shows more-significant amounts of potential swell (up to 60%).

- The swell/shrinkage response of clay minerals is strongly dependent on the initial water content (hydration state) of the material.

- The physiochemical swell of clay minerals due to CO2 exposure involves an interaction of CO2 and H2O; based on microfabric evidence, CO2 induced swell apparently can occur only over a limited range of hydration states depending on the clay mineral. Laboratory test data also suggest that there is a potential for shrinkage of shale due to the removal of H2O from clay minerals (i.e., dryout) due to CO2 dominant flow and (possibly) due to replacement by CO2.

- From microfabric studies on clay minerals, the swelling of montmorillonites is greater than that of kaolinites, and the swell of Ca-montmorillonite is greater than Na-montmorillonite or K-montmorillonite. At larger test scales, kaolinite and illite show little swell response to CO2.

- The swelling strain of mudstones exposed to CO2 has been observed to decrease with increasing temperature to a minor degree and to vary significantly with the type of wetting fluid.

- Overall, there is a lack of data on this topic, especially in lab-scale experimentation.

On Chemical Reactions:

- Exposure of mudstones to CO2 will induce reactions dominated by carbonic acid, particularly in reacting with minerals like dolomite and calcite. These reactions will be dependent on the mineralogy of the mudstone as well as the chemical composition of the ambient fluid/brine.

- Reactions to CO2 with mudstone including the dissolution of clay minerals and precipitation of secondary clay minerals have been observed over a wide temperature range (20 °C to 250 °C).

- Chemical reactions with mudstones occur rapidly with the introduction of CO2 and most mineralogical/ion/elemental changes become stable in tests after several days. However, continued, long-term reactions have been observed up to 5 years after the start of testing.

- A mixture of CO2 with brine (or water) is more reactive to mudstone than CO2 alone in causing alteration, dissolution, and precipitation. Exposure to CO2 alone (dry CO2) has a reduced effect on apparent mudstone response.

- Testing to date of the geochemical reactivity of CO2 has focused on CO2 dissolved in H2O, and no data on the effects of H2O dissolved in CO2 on mudstones have been systematically studied.

70 Contrary to common terminology, there is no designation of “swelling clays” as most clay minerals show some response to CO2 and H2O. However, montmorillonites evidence more swell than other clay minerals.
On Mechanical Response:

- Strength tests (UCS, point load, indirect tensile test) and compressibility measurements (Young’s modulus, Poisson’s ratio) on mudstones are affected by exposure to CO₂. The effects vary and depend on the duration and type of CO₂ exposure/aging.
- The effects of CO₂ exposure on mechanical properties of mudstones varies with sample fabric and the degree of anisotropy of a sample can change with exposure duration.
- The effect of swell induced by CO₂ on the mechanical response of mudstones could not be evaluated due to lack of data.

On Permeability:

- CO₂ exposure has a variable effect on the permeability of intact mudstones, and the effect increases with the duration of exposure. The effect also increases with the availability of water or brine.
- Fracture permeability tests have shown both increases and decreases in permeability with longer CO₂ exposure, which is apparently dependent on sample mineralogy and the flow path through the sample.
- The effect of CO₂ on the permeability of intact mudstones is influenced by the rock anisotropy.
- Especially with two-phase flow, CO₂ flow through an intact mudstone is along preferred pathways (connected porosity). These pathways are expected to be the fastest travel paths in the sample fabric but as such may not include all large voids. These preferred pathways can also be expected to experience the largest amount of alteration.
- The CO₂ gas permeability of intact mudstone samples decreases with increasing pore/gas pressure. Single-layer propped fractures have also shown a decrease in gas permeability with CO₂ with increasing gas pressure. Conversely, the CO₂ gas permeability of artificial (or clean) fractures in mudstone exhibit increasing permeability with increasing gas pressure.
- Current methods of fracture permeability testing have several limitations in simulating uniform loading conditions.

4.2 RECOMMENDATIONS

In the main body, this report provides several observations integral to construct a more comprehensive understanding of shale behavior in future research. However, the following actions are considered of paramount importance:

1. Performing swell testing of mudstones with CO₂ on larger scale samples. There are insufficient data on this topic to support engineering applications. This testing will also require the development of new methods and test standards, as for example, to limit corrosion with CO₂-brine mixtures.
2. Refining test methodology and equipment for the sorption testing with CO₂. This is required to eliminate negative excess sorption results (an apparent error) in tests and to enhance repeatability.
3. **Characterizing samples before and after testing.** The mineralogy, water content, and microfabric of the samples are fundamental to understanding the response of a mudstone and should be measured in an experimental program. To evaluate the extent of sample alteration during swell testing at a lab-scale requires sectioning and full examination after testing to evaluate the efficiency and uniformity of the treatment process across the core. This also requires water content determinations before, during, and after testing.

4. **Ensuring that the saline or brine solution used in testing is chemically neutral with shale.** A reactive solution can mask the actual response to CO$_2$ together with the solution, potentially introducing substantial errors in conclusions. Hence, the solution (representing the existing in situ brine) used in swell-related tests should be formulated to be as nonreactive as possible, and the solution alone should be tested with the mudstone to separate and quantify the effects of adding CO$_2$ to the rock mass in situ.

5. **Minimizing sample disturbance** (especially the loss of moisture during sample storage) prior to and during testing to obtain a more accurate prediction of field response. Disturbance such as drying can incorrectly emphasize the extent of swell behavior, potentially creating a problem where none exists.  

6. **Quantifying the effect of non-uniform surface loading** in the fracture permeability testing of axial shale samples. This quantification may require performing radial flow testing of larger samples or use of cubic samples to obtain data in comparison to axial sample tests.

7. **Incorporating the potential for property variability in the modeling shale units.** A uniform, homogeneous shale or mudstone layer should not be assumed in considering the unit to function as a caprock. The permeability, fabric, and thickness of the unit will vary with location. Not assessing the variability of these units can lead to major problems in engineering applications.

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71 There may also be aspects of thermal history influencing sample disturbance (e.g., temperature changes from in situ inducing sample contraction, or expansion due to testing at elevated temperatures). However, no data on this topic were found.

72 A radial flow test allows the application of uniform axial load across the surface.
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APPENDIX A: DETAILED DESCRIPTIONS OF CO₂ SORPTION TESTING

A.1. SORPTION TEST SUMMARIES

A.1.1. CO₂ SORPTION BY CLAY MINERALS

Brief summaries of relevant experimental results of CO₂ sorption on clay minerals are discussed in this section. Clay mineral testing is often performed using so-called “standard” clay types obtained from the Clay Minerals Society. For reference, these standard clay samples are identified with the symbol nomenclature shown in Table A1.

The summaries in this appendix include Venaruzzo et al. (2002), Busch et al. (2008), Pribylov et al. (2010), Heller (2013), Heller and Zoback (2014), Romanov (2013), Rother et al. (2013), Jeon et al. (2014), Schaef et al. (2014a, 2014b, 2015), and Kumar (2016). These summaries focus on describing experimental conditions, sample origin, and mineralogy, and the results of the testing of sorption on clay minerals by each author in contrast to a typical abstract.

In chronological order, the following sections describe CO₂ sorption testing on clay minerals:

Venaruzzo et al. (2002) conducted sorption tests on two bentonite clay minerals from Patagonia, Argentina using CO, CO₂, and sulfur dioxide (SO₂) gases. The samples were from the Collón Curá Formation of the Upper Miocene, province of Neuquén, and were labeled M1 (altered tuffaceous material containing bentonite clay) and M4 (bentonite from the diagenetic alteration of andesitic tuff). Tests were conducted at 25 °C and at a pressure of 0.098 MPa, and conducted on treated and untreated samples. The treated clay mineral samples were modified with 3.0 and 6.0 M hydrogen chloride (HCl) solution at boiling temperature over 3 hours. Three tests were performed on the untreated and on treated samples of the two clays (i.e., for a total of 12 tests). The acid treatment removed the interlayer cations such as Ca²⁺, Na⁺, and K⁺, as well as octahedral cations of the smectite clays.

Results indicated that equilibrium adsorption of CO₂ was approximately 50% of that for SO₂, but greater (by a factor of 3 to 4) than for CO sorption for both natural and treated samples (i.e., SO₄ sorption > CO₂ sorption > CO sorption). For untreated samples, CO₂ adsorption for M1 clay ranged from 0.230 to 0.384 mmol/g while for M4 clay sorption ranged 0.218 to 0.308 mmol/g (note that M4 had a greater smectite content). The gas adsorption values...
increased after acid treatment (except for one sample with CO), and could be attributed to structural and textural properties.

**Busch et al. (2008)** performed tests on four clay minerals at pressures up to approximately 12 MPa and at a temperature of 45 °C. The clay minerals were (1) Ca-rich montmorillonite (STx-1b), (2) Na-rich montmorillonite (SWy-2), (3) illite (IMt-1), and (4) kaolinite (KGa-1b), all of which were obtained from the Clay Minerals Society. The sorption capacity of powdered clay samples was determined as a function of pressure by a manometric method. Some samples were dried under vacuum at 105 °C for at least 90 min prior to testing.

From obtained data, the tests on the clay minerals conducted by Busch et al. (2008) generally show an asymptotic shape of increasing excess sorption with increasing pressure up to a pressure of about 8 MPa; the shape is traditionally termed a Langmuir isotherm (e.g., Clarkson and Haghshenas, 2013). However, above 8 MPa, the isotherms deviate from this trend and show a sharp decline, (asymptotically) reaching a reduced sorption value less than about half the peak value (see Figure A1a).

In review of these isotherms, the Ca-montmorillonite mineral adsorption isotherms are significantly higher than those of the other clay minerals at the same pressure, with a peak value of approximately 1.2 mmol/g for the as-received sample. The remaining as-received samples of Na-montmorillonite, illite, and kaolinite have a peak excess sorption of only 0.6 mmol/g, 0.3 mmol/g and 0.2 mmol/g, respectively. In addition, dried samples of Ca-montmorillonite, Na-montmorillonite, and illite appear (at least initially) to show an increased adsorption in comparison to the as-received sample.

As an exception to the general trend, the kaolinite samples show a more variable pattern at higher pressures from the other results, as shown in Figure A1b. The kaolinite as-received sample shows a more erratic trend (a peak) at approximately 10 MPa, and is variable in trend afterward. Further, the tested dried sample for kaolinite also shows significantly lower sorption than the as-received sample, a reversed trend from the other minerals. However, it is noted that the as-received water content of 0.1% of this sample is considered very low, and this result may not representative.

In addition, for a retest of the as-received kaolinite sample, the second cycle sorption is substantially reduced, but still maintains an erratic trend at 10 MPa and variable response as for the first cycle. In addition, below 10 MPa, the second-cycle sorption is similar in magnitude to the sorption of the dried sample (Figure A1b).
### Table A1: Selected Clay Sample Abbreviations - Clay Minerals Society

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>STx-1 / STx-1b*</td>
<td>Ca-Montmorillonite (Texas); Origin: Manning Formation, Jackson group (Eocene), Gonzales County, Texas, USA; major exchange cation: Ca,</td>
</tr>
<tr>
<td>SWy-1, SWy-2, SWy-3*</td>
<td>Na-Montmorillonite (Wyoming); Origin: Newcastle Formation, (Cretaceous), Crook County, Wyoming, USA; principal exchange cations Na and Ca</td>
</tr>
<tr>
<td>SCa-3*</td>
<td>(Special) Montmorillonite (California) (bentonite and traces of illite): Origin: Otay Formation (Oligocene(?)), San Diego County, California, USA; (high charge)</td>
</tr>
<tr>
<td>IMt-1, IMt-2</td>
<td>Illite; Origin: Cambrian shale, Silver Hill Formation, Jefferson Canyon, Montana, USA.</td>
</tr>
<tr>
<td>KGa-1 (KGa-1b*)</td>
<td>Kaolinite (low defect); Origin: Tuscaloosa Formation (?) (Cretaceous(?)) (stratigraphy uncertain), Washington County, Georgia, USA</td>
</tr>
<tr>
<td>KGa-2*</td>
<td>Kaolinite (high defect); Origin: lower tertiary (stratigraphic sequence uncertain), Warren County, Georgia, USA</td>
</tr>
<tr>
<td>PFl-1*</td>
<td>Palygorskite; Origin: Hawthorne Formation, (Miocene), Gadsden County, Florida, USA</td>
</tr>
<tr>
<td>SHCa-1*</td>
<td>Hectorite, Origin: Red Mountain Andesite Formation (Pliocene), San Bernardino County, California, USA</td>
</tr>
<tr>
<td>SepSp-1*</td>
<td>(Special) Sepiolite (meerschaum); Origin: (Miocene) Valdemoro, Spain; contains minor calcite.</td>
</tr>
</tbody>
</table>

Source: Based on CMS (2016a, 2016b).

Notes:
- * = Source material available on 9/6/2016.
- ? = data uncertain.
Notes:

b Tests conducted at 45 °C. Some tests were conducted twice on the same sample. Sample water contents are given at the start of the test; other samples were oven dried before the test.

c Abbreviations: a.r. = as received at the laboratory; Ca = calcium; dry = sample dried at 105 °C for 90 minutes prior to test; montm = montmorillonite; Na = sodium; w.c. = water content at start of test.

Figure A1: Excess adsorption of CO₂ on clay minerals from Busch et al. (2008).
**Pribylov et al. (2010)** performed CO₂ (subcritical) sorption testing on specially-prepared Na-montmorillonite samples at temperatures of approximately 30 °C, 70 °C, 100 °C, and 127 °C\(^{77}\) and at pressures ranging from 0.1 to 6.0 MPa. The source samples were Azkamar white bentonite from Uzbekistan. One sample was used without treatment (abbreviated NaMt). The second, a pyridinium form of montmorillonite (abbreviated PyMt), was prepared by treating 2% bentonite suspension with a 0.02 N aqueous pyridine hydrochloride solution. The third, a polyhydroxyaluminum form of montmorillonite (abbreviated PHAMt) was prepared by treating a suspension of the white bentonite with a hydroxyaluminum complex.\(^{78}\)

All obtained sorption isotherms exhibited a Langmuir isotherm shape, with a peak sorption at 6 MPa. The untreated sample, NaMt, had a peak sorption of approximately 0.8 mmol/g at 30 °C, decreasing with temperature to approximately 0.4 mmol/g at 127 °C. The PyMt samples had a peak of approximately 1.6 mmol/g at 30 °C, decreasing to approximately 1.2 mmol/g at 127 °C. The third material, PHAMt, peaked at approximately 1.0 mmol/g at 30 °C, decreasing to approximately 0.6 mmol/g at 127 °C. The rate of temperature dependence in these tests appeared to decrease with increasing temperature. The authors concluded that the character of CO₂ adsorption on NaMt and PHAMt is analogous to the adsorption on a smooth surface, whereas PyMt behaves as a microporous adsorbent.

**Heller (2013) and Heller and Zoback (2014)** performed CO₂ and CH₄ adsorptive capacity measurements with illite and kaolinite on samples\(^{79}\) obtained from the Clay Mineral Society, as well as kerogen, at a temperature of 40 °C and at pressures up to 8 MPa. Sorption was determined using a volumetric method, and samples had a grain size of 50 and 150 µm.

The maximum CO₂ sorption value of 161.2 scf/ton was reported for the illite and 114.4 scf/ton for the kaolinite. The isotherms for the absolute adsorption tests generally showed a Langmuir isotherm shape with increasing sorption and with increasing pressure (Figure A2). The results indicated in all cases, that the CO₂ sorption was significantly greater than CH₄ sorption. The CO₂ sorption for the illite and kaolinite samples were greater by a factor of 1.2 and 3.6 than the CH₄ absorption, respectively. For CO₂, the sorption by illite was approximately twice the sorption by kaolinite at the same pressure.

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\(^{77}\) Temperatures converted from K to °C for consistency; values shown include a rounding difference of 0.15 °C.

\(^{78}\) The specific method of sample preparation was not described in the paper.

\(^{79}\) The specific type/source of the clay minerals was not mentioned. The activated carbon (Filtrasorb 400, 12 x 40 mesh) was purchased from Calgon Carbon as representative of mature kerogen.
Romanov (2013) conducted an experimental investigation on the adsorptive capacity of Ca-montmorillonite (STx-1b) and Na-montmorillonite (SWy-2) samples as received from the Clay Mineral Society. Tests were conducted at variable temperatures. Initially, the samples were pressurized at a temperature of 50 °C up to about 10 MPa, then subsequently heated to greater than 90 °C and pressurized to greater than 17 MPa. The samples were then finally cooled to 55 °C and slowly depressurized to determine residual sorption.

Isotherms for all adsorption tests generally showed an increasing sorption up to pressures of about 11 MPa (Figure A3), with Ca-montmorillonite sorbing more CO₂ than Na-montmorillonite. At higher pressures, the sorption curves decreased, and depressurization indicated hysteresis and a residual sorption value. Na-montmorillonite had a peak excess sorption of about 0.85 mmol/g, and Ca-montmorillonite had a peak excess sorption of about 1.35 mmol/g. The sorption/pressurization curves have a general Langmuir isotherm shape, similar in trend to that of Heller and Zoback (2014).

Rother et al. (2013) conducted adsorptive capacity tests with CO₂ on treated montmorillonite (STx-1) obtained from the Clay Minerals Society. In preparation, samples were first reacted with 1 M sodium acetate (C₂H₃NaO₂) solution to replace Ca ions. After removal of excess acetate, samples were separated to retain only the clay-sized fraction (less than 2 μm). The samples were subsequently washed with deionized water.
Notes:

\(^a\) Tests were initially conducted at 55 °C on as-received powders. The samples were subsequently heated to above 90 °C, then cooled to 55 °C and slowly depressurized to determine residual sorption.

Figure A3: Adsorption of CO\(_2\) on clay minerals from Romanov (2013).

Then suspensions were flocculated with 5 M sodium chloride (NaCl) solution, followed by removal of excess NaCl by dialysis, and freeze-drying. Excess sorption testing was performed using a gravimetric technique and neutron diffraction. Bulk fluid densities of CO\(_2\) obtained indirectly from pressure measurements using an equation of state. Tests were conducted at temperatures of 35 °C and 50 °C and over a pressure range of 0 to 20.0 MPa.

As stated by the authors, the maximum excess sorption of Na-montmorillonite was approximately 0.025 g of CO\(_2\) versus each g of clay sample (g/g) at a temperature of 50 °C, and approximately 0.030 g/g at 35 °C. The maxima occurred at pressures of 5.8 MPa (35 °C) and 6.4 MPa (50 °C) (i.e., at a CO\(_2\) bulk density of approximately 0.15 g/cm\(^3\)). After peaking, both excess sorption isotherms decline and become negative at a bulk density of 0.32 g/cm\(^3\) (at 50 °C) and 0.42 g/cm\(^3\) (at 35 °C) with a continuing steady decrease in sorption up to bulk densities of 0.7 to 0.8 g/cm\(^3\).

In review of test results, a small temperature effect is apparent, with sorption results somewhat lower at 50 °C than at 35 °C.

\textbf{Jeon et al. (2014)} conducted adsorptive capacity tests with CO\(_2\) on samples of illite (IMt-1), montmorillonite (SCa-3), and sepiolite, (SepSp-1) all of which were obtained from the Clay Minerals Society. Tests were performed at 45 °C and 55 °C, up to pressures of 12 MPa. Prior to testing, the samples were gently ground to a particle size of 150 to 500 μm and dried.
Experiments were performed using a gravimetric method with a magnetic suspension balance.

Upon pressurization, excess sorption isotherms for montmorillonite increased with pressure and peaked at about 7 to 8 MPa, and then decreased with peak values excess-sorbed CO$_2$ of about 0.8 to 1.0 mmol/g (see Figure A4). Upon depressurization, the sorption values increased significantly to about 1.4 mmol/g at about 4 to 5 MPa and then decreased only slightly, with a residual excess sorption about 1.0 mmol/g. For illite, the peak sorption was significantly smaller and showed little hysteresis between pressurization and depressurization, with a peak sorption of about 0.18 to 3.0 mmol/g at 4 MPa.

The sepiolite samples (hydrous magnesium silicate, also known as meerschaum) showed the largest CO$_2$ excess sorption over the entire pressure range with a peak value of approximately 3.3 mmol/g, with little to no difference in the isotherms for the two temperatures, similar to illite.

For montmorillonite samples, a small difference between the two isothermal curves at 45 °C and 55 °C is evident, suggesting a decreasing trend in sorption with increasing temperature for this material. However, the differences between the two isothermal curves for both illite and sepiolite can be considered negligible.

Schaef et al. (2014b) conducted CO$_2$, N$_2$, and He sorption tests on kaolinite using a quartz crystal microbalance and density functional theory methods. The authors used clay mineral samples of kaolinite (KGa-2) obtained from the Clay Minerals Society. Tests were conducted as a function of pressure up to 12.5 MPa at a temperature of 50 °C. Polished, gold-coated 10 MHz quartz crystals were coated with kaolinite (less than 2 μm grain size) by pipetting a dilute slurry containing approximately 5.14 μL/g of clay directly onto the gold electrode portion and tested. Samples were air dried prior to testing.

In examining the results for N$_2$ and He, the two sorption isotherms produced similarly shaped profiles with the total amounts of absorbed gas showing essentially pressure-independent response as noted by the authors. In contrast, the measured sorption of CO$_2$ on kaolinite indicated a pressure-dependent response with CO$_2$ concentrations first increasing with increasing pressure until reaching a maximum at a density corresponding to about 0.40 g/cm$^3$. Subsequently, surface concentrations of CO$_2$ decreased with increasing pressure. As stated by Schaef et al. (2014b), the peak sorption was approximately 0.9 to 1.2 mmol of CO$_2$/g.
Schaef et al. (2014a) conducted CO₂, N₂ and CH₄ sorption tests on dehydrated Na-montmorillonite using a quartz crystal microbalance and density functional theory methods. The authors used clay mineral samples of montmorillonite (Na-SWy-2) obtained from the Clay Minerals Society. Tests were conducted as a function of pressure up to 12.5 MPa at a temperature of 50 °C.

From test results, it is evident that the sorption for both N₂ and CH₄ increase essentially linearly throughout the pressure interval for the testing and achieve peak concentrations of 0.4 and 0.6 mmol/g of clay, respectively. In contrast, the CO₂ sorption increases almost linearly to 5 MPa, then increases sharply, showing a ragged maximum at about 9 MPa and decreasing at higher pressures (at about 10 MPa) to the end of test (Figure A5).
Schaef et al. (2015) conducted CO₂, N₂ and CH₄ sorption tests on specially prepared montmorillonite samples using a quartz crystal microbalance and density functional theory methods. The authors used clay mineral samples of Na-montmorillonite (SWy-2) and Ca-montmorillonite (STx-1) obtained from the Clay Minerals Society as source materials. Subsequently, the fines fraction (grain size less than 2 μm) of SWy-2 were saturated with Ca²⁺, Na⁺, and magnesium ion (Mg²⁺) solutions, and STx-1 was saturated with Ca²⁺. This produced homoionic samples referred to as Ca-SWy-2, Na-SWy-2, Mg-SWy-2, and Ca-STx-1, respectively.

Sorption tests on selected samples were conducted as a function of pressure up to 12.5 MPa at a temperature of 50 °C. Sets of isotherms were generated for two materials: (1) Ca-SWy-2 and (2) Na-SWy-2. The authors note that the Na-SWy-2 (0W) isotherms recorded only external CO₂ adsorption whereas Ca-SWy-2 (sub-1W) sorbed CO₂ on external surfaces and in the interlayer region.

The resulting isotherms differ by clay type (see Figure A6). The isotherms of Na-SWy-2 samples increase in sorption with increasing pressure, but with a generally increasing rate, and peak at pressures above 9.5 MPa, and then decrease. The average peak value is about 0.45 mmol/g.

The Ca-SWy-2 samples evidence an increase in sorption with pressure (a typical Langmuir isotherm shape) up to a pressure of about 7 MPa, then show a sharp increase in rate and a peak at about 9.5 MPa. Sorption then decreases with higher pressures. The peak sorption for Ca-SWy-2 is significantly larger than for Na-SWy-2, averaging 1.26 mmol/g at approximately 9.0 MPa.
Kumar (2016) conducted CO\textsubscript{2} sorption tests on an illite sample and on Bakken Shale samples (the mudstone testing is described later) in both dry and water-imbibed states. The illite was obtained from the Clay Minerals Society.\textsuperscript{80} Before testing, both the dry and water-imbibed clay samples were degassed for about 24 hours under a vacuum at 150 °C temperature. The water-imbibed sample was then pressure-saturated at 28 MPa (4,000 psi) for 48 hours. Sorption tests were conducted on the illites at a temperature of 50 °C, at pressures varying up to 11 to 12 MPa (1,600 to 1,800 psi).

The isotherms for the dry samples versus water-imbibed illite samples differ significantly. In the dry condition, the excess sorption isotherm increases significantly with pressure, and exhibits a typical Langmuir type shape with a peak value of approximately 3.5 mmol/g. The water-imbibed illite, however, has a much-reduced excess sorption and shows little change with pressure; this sample has a maximum value of only 0.1 mmol/g. No significant decrease in excess sorption is apparent over this pressure range as shown by Kumar.

### A.1.2. CO\textsubscript{2} SORPTION BY SHALES / MUDSTONES

Relevant experimental results for CO\textsubscript{2} sorption testing with very-fine-grained sedimentary rock (generally termed shale or mudstone) are provided in this section as a basis for discussion in the

\textsuperscript{80} The specific type/source of the clay mineral was not mentioned.
main body of the report. The testing summaries of shales and mudstones include Nuttall et al. (2003, 2005), Busch et al. (2008), Busch et al. (2009), Kang et al. (2010, 2011), Weniger et al. (2010), Wollenweber et al. (2010), Charoensuppanimit et al. (2012), Heller (2013), Heller and Zoback (2014), Khosrokhavar (2014), Khosrokhavar et al. (2014), Gasparik et al. (2014), Schaef (2015), Dilmore et al. (2015), Luo et al. (2015), Hong et al. (2016), Charoensuppanimit et al. (2016), Duan et al. (2016), Kumar (2016) and Meray and Sinayuc (2016). The summaries focus on describing experimental conditions, sample origin and mineralogy and the results of the testing of sorption on mudstones.

In chronological order, the following sections describe CO2 sorption testing on shales and mudstones:

**Nuttall et al. (2003, 2005)** conducted a series of adsorptive capacity tests with CH4 and CO2 on several units of carbonaceous (black) Devonian gas shales from Kentucky over a range of pressures at 30 °C. The shale samples contained 30 to 75% clay minerals, composed of mixed-layer clays (illite-smectite and illite-chlorite), chlorite, and kaolinite. Testing used cuttings as well as intact sidewall core.

Isotherms in Figure A7 are shown for a pressure range up to 8.3 MPa (2,000 psi). The CO2 adsorption of these samples was found to range from 14 to 136 scf/ton with a median value of 40 scf/ton at conditions of 2.75 MPa. In contrast, the adsorption capacity is significantly lower for CH4 (shown in red in Figure A7), which ranged only from 2 to 38 scf/ton with a median value of 8 scf/ton at similar conditions. It is noted that the mean CO2 adsorption is 5 times the CH4 median adsorption.

These test results demonstrate that the sorption of CO2 by shale is pressure-dependent, and this relationship is highly non-linear below about 2.8 MPa (400 psi). The authors also noted that over the range of organic content of 0.69 to 14.7% of the test samples, there was a very good correlation between the measured total organic carbon content and the CO2 adsorptive capacity of the sample.

Nuttall et al. (2005) expressed this experimental relationship of the CO2 (gas) adsorptive capacity $G_{SCO2}$, as a function of the organic content as:

$$G_{SCO2}[\text{scf/ton}] = (7.9 \times TOC) + 20.7 \ [\text{at 400 psi}]$$

where TOC is the total organic content (in percent).
Review of the Effects of CO₂ on Very-Fine-Grained Sedimentary Rock/Shale - Part III Shale Response to CO₂

Notes:

a Test conducted at 30 °C on carbonaceous (black) Devonian gas shales.
b 1,000 psi = 6.895 MPa.
c Y-Axis should be titled “Adsorbed Gas”, not CO₂. Red lines are for CH₄, black for CO₂.

Figure A7: Adsorption of CO₂ and CH₄ on gas shales from Nuttall et al. (2005).

This relationship when expressed in metric units becomes (Weniger et al., 2010):

\[
GSC_{CO₂}[\text{mmol/g}] = (0.009 \times TOC) + 0.025 \text{ (at 2.76 MPa)}
\]  

Busch et al. (2008) performed tests on powdered Muderong Shale from Australia at a temperature of 50 °C, at pressures up to 25 MPa. The shale had a low organic content (less than 0.5%) and a significant clay content (66%), composed of illite-smectite, smectite, mica/illite, and kaolinite. It was observed that the shale samples did dry to some degree during the sampling process, but the samples were coated with a mineral oil to inhibit further drying when logged and stored. Some shale samples were intentionally dried in the laboratory before testing.

Test results for the shale are shown in Figure A8. The authors noted that the shape of the isotherms for all runs differ significantly from “normal” gas sorption isotherms with a single

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84 Samples were from a depth of 1,454 m below the seafloor.
85 Dried at 105 °C for 90 minutes.
trend; and the authors proposed segmenting the curve into three parts, defining different regions along the curves at bounds of about 7 and 12 MPa.

In addition, the adsorption on the first run peaks at a value of about 0.95 mmol/g at 12 MPa. However, the second run shows a significant decline in the peak adsorption value (about 0.55 mmol/g) from the first run at 12 MPa, and differs in shape as well as magnitude. In addition, the second run evidences a distinct trough at about 9.2 MPa before the peak at 12 MPa. Further, the dried sample curve, while it replicates the trend of the second run, shows adsorption values lower than both the as-received tests, especially at higher pressures, and the curve peaks somewhat earlier. This difference indicates a decrease in sorption with increasing water content at higher pressures, especially at pressures greater than 12 MPa.

The authors conclude that given the low organic content of the shale and the sorption evident for clay minerals, the measurements show that the CO2 sorption capacity of the Muderong Shale may be attributed entirely to its clay minerals constituents.

![Excess adsorption of CO2 on Muderong Shale](image_url)

Source: Busch et al. (2008)

Notes:

a Test conducted on Muderong Shale at 50 °C; samples “as received” (a.r.) water content is 3.34%. The second run is performed on the same sample.

b Abbreviations: a.r. = as received at the laboratory.

Figure A8: Excess adsorption of CO2 on Muderong Shale from Busch et al. (2008).
Busch et al. (2009) reported testing on shale from Warndt-Luisenthal, Germany, in addition to testing data provided earlier by Busch et al. (2008) on Muderong Shale. The Paleozoic Warndt-Luisenthal Shale was from an underground coal mine in the Saar area. Gas sorption experiments were performed on three samples at differing water content at 50 °C. Samples were powdered to a grain size of less than 200 μm.

Results of the Warndt-Luisenthal samples are shown in Figure A9. Initially, all samples show similar results to about 7 MPa. However, at higher pressures, the as-received and the moist samples show a definitive peak in the isotherms at about 10 MPa, with a moderate decrease thereafter. The dried sample shows no such peak and decreases rapidly to about zero excess sorption after 10 MPa.

These results indicate that (in contrast to clay mineral testing), the peak CO₂ sorption for this material apparently decreases with decreasing water content. This is also consistent with the Muderong sample from Busch et al. (2008) discussed earlier (see Figure A8).

![Figure A9: Excess adsorption of CO₂ on Warndt-Luisenthal Shale from Busch et al. (2009).](image)

Notes:

- Tests conducted at 50 °C. Sample material had an "as received" water content of 0.13%. For the "moist" test, the sample was wetted with (tap) water prior to testing.
- 1 kg/t ~ 17.48 scf/t for CO₂.

86 No mineralogical or petrophysical data for the Paleozoic shale was provided.
Kang et al. (2010, 2011) tested samples from core plugs\(^87\) and employed pressure pulse decay experiments to measure CO\(_2\) and CH\(_4\) adsorption on two organic-rich Barnett Shale samples. The organic content of the samples was 3% and 3.9%; the clay mineral content of the samples was not reported. The measurements were at pressures up to 13.8 to 27.6 MPa at room temperature\(^88\). The authors extrapolated their data to Langmuir isotherms for a CO\(_2\) adsorption capacity of 250 scf/ton at approximately 17 MPa pressure in one sample, and 590 scf/ton at approximately 22 MPa in the other. The isotherm curves shown for CO\(_2\) were substantially greater than the isotherm curves for CH\(_4\).

Weniger et al. (2010) conducted excess sorption capacity tests on pulverized\(^89\) coal and carbonaceous shale samples with CO\(_2\) and CH\(_4\). CO\(_2\) sorption testing on shale was conducted into two sample sets. One set of shale samples was tested at temperatures of 45 °C and at pressures up to about 25 MPa and another set was tested at 35 °C and at pressures up to about 7.5 MPa. Samples were tested as received and not dried before testing. The clay content of the samples was not noted, and sample depth was noted for only two of the shale samples (at approximately 600 m).

Sorption tests with CO\(_2\) on shale samples (at higher pressures and at 45 °C) showed an excess sorption capacity in initially increasing with increasing pressure and peaking at about 8 to 10 MPa, (with some samples exhibiting a sharp peak) and then sharply decreasing thereafter at higher pressures. Peak values ranged from 0.14 to 0.54 mmol/g with the samples with higher TOC having an increased excess sorption isotherm and a significantly higher peak value (Figure A10). Tests at 35 °C and at lower pressures (up to 7.5 MPa) show no peaks; sorption capacity in these tests increased with increasing pressure to asymptote at about 7.5 MPa. Excess sorption values ranged from approximately 0.35 mmol/g to 0.85 mmol/g.

Similar to Nuttall (2005), the authors expressed an experimental relationship of the maximum CO\(_2\) excess (gas) sorption capacity, \(GSC_{CO_2}\), on shale as a function of the total organic content, (TOC), as:

\[
GSC_{CO_2}[\text{mmol/g}] = (0.008 \times TOC) + 0.183 \quad [\text{at 8 to 12 MPa}]
\]

where TOC is the total organic content (in percent).

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\(^{87}\) The preparations and dimensions of the samples are not described by the authors.

\(^{88}\) Temperature not stated by Kang (2010, 2011), but inferred from experimental description.

\(^{89}\) Sample grain size less than 0.2 mm.
Notes:

- Tests conducted at 45 °C.
- Individual data points are shown from testing, with lines showing an equation fit to data by authors.
- Samples are from the Irati and Ponta Grossa Formations. Samples from the Irati Formation have typically a higher total organic content (typically 8 to 13%) than the samples from the Ponta Grossa (typically 1.5 to 2.5%).

Figure A10: Excess adsorption of CO₂ on carbonaceous shales from Weniger et al. (2010).

Wollenweber et al. (2010) conducted CO₂ sorption tests with a marlstone and a limestone. Tests on the marlstone were conducted at 45 °C and at pressures up to 20 MPa. The sample was from a core taken at a depth of 128 m within the Emscher Marl Formation in the Münsterland Basin, Germany. The unit has a TOC of 0.4%, a calcite content of about 56% together with a clay content of roughly 21% (14% smectite, 7% mica/illite). Tests were performed on crushed samples with as-received water content. As observed, the isotherm increased rapidly with pressure to a peak excess sorption of 0.27 mmol/g at about 8.5 MPa, but then decreased sharply to 0.05 mmol/g at 10 MPa. The isotherm continued to decline thereafter, to zero at about 15 MPa, and became slightly negative at higher pressures.

Chareonsuppanimit et al. (2012) used pulverized, New Albany Shale samples to study sorption with CO₂, CH₄, and N₂ over a range of pressures at a temperature of 55.5 °C. The sample had a grain size less than 0.2 mm. Pulverized to a 250 µm size; samples from a depth of 1,384 to 1,385 m below grade.
samples were from the Grassy Creek Member of the New Albany group taken roughly at a depth of 1,380 m within the Illinois Basin and had a TOC of about 5.5% and a water content of 0.4%. The sample was cored in 1997 and stored in the intervening years.

The authors determined a CO$_2$ adsorption capacity of 0.1085 mmol/g for the unit at about 7 MPa. In addition, over a range of pressures of 1.7 to 12.6 MPa, the adsorption by the shale first increases then decreases at higher pressures (see Figure A11). The CO$_2$ adsorption, initially at a value of 0.0479 mmol/g at 1.7 MPa, increases with increasing pressure up to 9.75 MPa with a peak value of 0.1179 mmol/g, and then decreases at higher pressures to a value of 0.0942 mmol/g at 12.6 MPa (as stated by Chareonsuppanimit et al., 2012). The authors’ model (represented by the lines in Figure A11) diverge somewhat from the actual data points and this summary.

![Image](image.png)

Source: Chareonsuppanimit et al. (2012)

Notes:
- Diamonds represent CO$_2$ results, circles represent CH$_4$, and triangles represent N$_2$. The solid line is a model fit to data.
- Tests conducted at a temperature of 55.5 °C.

**Figure A11: Excess adsorption of CO$_2$, N$_2$, and CH$_4$ on New Albany Shale from Chareonsuppanimit et al. (2012).**

Other test results indicated that CH$_4$ sorption was only about 35% of the CO$_2$ sorption on Albany Shale and that N$_2$ was only about 11% of the CO$_2$ sorption at about 7 MPa. Further, the authors noted that the measured CO$_2$ adsorptive capacity on shales to be 10 to 30 times lower than CO$_2$ sorption on coals (as compared to data from Mohammad et al., 2012). The

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92 The mineralogy of the sample was not reported.
authors presumed that the lower value of CO₂ sorption in shale (versus coal) was due to the lower organic content (5%) and the higher ash content (89.4%) of this shale unit versus coal.

**Heller (2013) and Heller and Zoback (2014)** performed adsorptive capacity measurement on four types of crushed gas shale (mudstone) samples at a temperature of 40 °C and at pressures up to 12 MPa. The gas shale samples were from the Barnett, the Eagle Ford, the Marcellus and the Montney reservoirs. The total clay mineral content was 5.0%, 24.1%, 34.7% and 52.0% for the Eagle Ford, Montney, Barnett and Marcellus samples, respectively. The TOC for the samples ranged from 1.2% to 5.3%. Of note, the Eagle Ford sample had a high carbonate content (about 81%).

The CO₂ sorption values for the mudstones all exhibited a Langmuir isotherm shape and were reported as 147.4, 33.1, 63.7, and 153.0 scf/ton for the Barnett, Eagle Ford, Marcellus, and Montney samples, respectively (Figure A12). The results indicated that the CO₂ sorption was significantly greater than CH₄ sorption in all cases. The peak CO₂ sorption on the shales (mudstones) samples was greater by a factor of 1.9 to 2.8 than for CH₄ sorption.

The isotherms for all adsorption tests generally show a constant trend, with increasing sorption with a decreasing slope with increasing pressure and eventually appearing to asymptote to a value at higher pressures (i.e., resembling a Langmuir isotherm). In review of their results, Heller and Zoback (2014) concluded that they could not readily describe the shale gas samples’ adsorption isotherms as a sum of the isotherms of the mineral constituents. They also concluded that the adsorption values for shale were relatively small and sorption could prove relatively unimportant in gas production.

**Khosrokhavar (2014) and Khosrokhavar et al. (2014)** conducted CO₂ and CH₄ adsorption tests on pulverized Belgium dry black shale at pressures up to 10.5 MPa. The black shale has an organic content of 6.6% and contains 53% clay minerals, including illite (32.2%), kaolinite (16.1%) and chlorite (5.7%). Testing with CO₂ was performed at a temperature of 44.9 °C and with CH₄ at temperatures of 34.9, 44.9 and 62.9 °C.

Results of the two experiments with CO₂, the excess adsorption isotherm initially resembled a typical Langmuir isotherm curve for both samples (Figure A13) with values first increasing with increasing pressure to a peak at about 5.5 MPa. However, the at higher pressures, the isotherms rapidly decreased to zero (at 8 MPa), and then become negative thereafter. Peak values obtained for CO₂ were 0.153 and 0.175 mmol/g.

The authors indicated that the negative values (which have also been recorded by others) are possibly due to (1) overestimation of the void using He; (2) the finite density of the sorbed phase; (3) reaction of CO₂ with the minerals in the shale; (4) changing of the void volume during the experiment; and/or (5) the behavior of CO₂ near the critical point.

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93 Samples crushed to a particle size of between 50 and 150 µm
94 From British Columbia, Canada.
95 Samples were pulverized to 40 to 100-µm; and were from a depth of 745 m.
Notes:
\( a \) Triangles represent CO\(_2\) results, circles represent CH\(_4\). Tests conducted at a temperature of 40 °C.
\( b \) 1,000 psi = 6.895 MPa.

**Figure A12:** CO\(_2\) and CH\(_4\) absolute adsorption isotherms on various petroleum shales from Heller and Zoback (2014).

Notes:
\( a \) Tests conducted at a temperature of 49.9 °C.
\( b \) 10 bar = 1.0 MPa.

**Figure A13:** CO\(_2\) excess adsorption isotherms on Belgium dry black shale from Khosrokhavar (2014).
Three tests by these authors with CH\textsubscript{4} show a temperature-dependence, as peak values of excess sorption substantially decreased with increased temperature over the range 35 °C to 63 °C. In addition, the two higher temperature tests (at 44.9 °C and 62.9 °C) show a similar pattern to CO\textsubscript{2}, increasing to a peak value and then decreasing to zero and becoming negative.

Gasparik et al. (2014) described the results of an inter-laboratory study of high-pressure gas sorption measurements with different gases on two carbonaceous mudstones\textsuperscript{96} including sorption tests with CO\textsubscript{2}, CH\textsubscript{4}, and ethane (C\textsubscript{2}H\textsubscript{6}). Tests were performed on two units, (1) Namurian Shale and (2) Posidonia Shale, by different laboratories using differing techniques. The Namurian Shale is from Belgium and has a moderate organic carbon content of 4.4% and a total clay content of 40.3% in contrast to the Posidonia Shale from Germany, with an organic content of 15.1% and a clay content of only 20.3%. The samples were powdered\textsuperscript{97} and dried prior to testing.\textsuperscript{98} Tests were conducted at temperatures of 65 °C and gas pressures up to 25 MPa.

The test results with CO\textsubscript{2} for the two mudstones from the differing laboratories were generally comparable (see Figure A14 and Figure A15). The Posidonia Shale results show slightly higher peak values with a significantly higher organic content and lower clay content. Numerically, the results up to 4 MPa for each rock unit are highly similar. However, results diverge for rock units above 7 MPa and there are differences in trend between certain laboratories. For example, the isotherms from Laboratories #5 and #6 show distinct peak values (at 10 to 12 MPa), while the others do not, for the same rock type. In addition, the test results from Laboratory #4 for Posidonia Shale become negative above 11 MPa (inset in Figure A15).\textsuperscript{99} Similarly, most isotherms from C\textsubscript{2}H\textsubscript{6} also show a distinct peak like CO\textsubscript{2}, but at a lower pressure (about 8 MPa\textsuperscript{100}), and then evidence a decrease thereafter. The CH\textsubscript{4} isotherms, however, show no such distinct peak or decrease in the isotherm curve.

Based on the entire study, Gasparik et al. (2014) concluded that the discrepancies in high-pressure sorption measurements are significant considering the sorption capacity of shales, and indicate that the current quality standards in measurement procedures need improvement, especially in identifying and eliminating the systematic errors.

\textsuperscript{96} Given the low clay content, these units are described as mudstones rather than shales; see discussion in Lindner (2016a).

\textsuperscript{97} The average particle size was less than 100 μm.

\textsuperscript{98} Each sample was subjected to a drying process at 110 °C under vacuum for 18 hours. In some cases, this was followed by additional drying of the sample in the sample cell at 110 °C, vacuum for 2 to 8 hours.

\textsuperscript{99} It was proposed that the negative results were a measurement artifact due to an inappropriate use of a less-accurate equation of state as well as due to cross-contamination of the CO\textsubscript{2} with He.

\textsuperscript{100} Ethane has a critical pressure of 4.9 MPa, and a critical temperature of 32.2 °C (NIST, 2016b), like but lower than, CO\textsubscript{2}. This suggests that the distinct peak is related to the phase change to a supercritical fluid.
Review of the Effects of CO₂ on Very-Fine-Grained Sedimentary Rock/Shale - Part III Shale Response to CO₂

Note:

a Test performed on Namurian Shale at a temperature of 65 °C; testing by various laboratories.

Figure A14: CO₂ excess adsorption isotherms of Namurian Shale from Gasparik et al. (2014).

Note:

a Test performed on Posidonia Shale at a temperature of 65 °C; testing by various laboratories.

Figure A15: CO₂ excess adsorption isotherms of Posidonia Shale from Gasparik et al. (2014).
**Schaef (2015):** illustrated results of testing sorption using a quartz crystal microbalance and density functional theory methods to determine CO₂ sorption on three clay fractions of a Woodford Shale sample.¹⁰¹ The sorption isotherms of three tests (with a second cycle shown for one test) are shown for pressures up to 14 MPa for tests conducted at 50 °C (Figure A16).

The initial part of the isotherms for all tests appear to linearly increase with increasing pressure up to a pressure of 6.5 MPa. At this point, sorption capacity increases dramatically, and peaks at a pressure of 9 to 10 MPa, then subsequently decreases rapidly, reaching a zero value at pressures of roughly 12 to 14 MPa. Peak sorption values range from 1.3 to 1.8 mmol/g (values comparable to clay mineral testing from Busch et al., 2008).

**Dilmore et al. (2015), Hong et al. (2016)** conducted various tests on several mudstone members of the Marcellus Shale Formation, including adsorption capacity measurements with CO₂ and CH₄. Samples were taken from outcrops in West Virginia, New York, and Pennsylvania. Based on available testing, the clay mineral content of the samples was

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¹⁰¹ Details of mineral content, sample source and sample preparation are not provided in the source reference. Woodford Shale contains quartz, illite, kaolinite, and smectite (McGrail et al., 2015).
primarily illite with some chlorite, and ranging from about 6% to 36%. Total carbon content ranged from 1.13% to 14.73% and the total organic carbon content from 0.4% to 8.9%. For CO₂ tests, powered samples were tested at pressures up to approximately 14.0 MPa at 76.1 °C. Tests with CH₄ were performed at pressures up to 34 MPa, at the same temperature.

As shown in Figure A17, maximum storage capacity values with CO₂ were measured at between 0.0739 to 0.3951 mmol/g. These sorption capacity isotherms increased with increasing pressure, but with a slowly decreasing rate over time. The isotherms continue to be increasing at 14 MPa and no asymptotic limits in the trends were apparent.

![Graph showing CO₂ adsorption data](source)

**Source:** Modified from Hong et al. (2016)

**Note:**

- Tests on mudstone members of the Marcellus Shale Formation at a temperature of 76.1 °C (Based on discussion with authors, figure captions in source reference are in error).
- 10 bar = 1.0 MPa; mol/kg = mmol/g.

**Figure A17:** CO₂ adsorption data on various mudstone members of Marcellus Shale from Hong et al. (2016).

Storage isotherms for CH₄ exhibited similar trend with maximum storage capacity values ranging from 0.0244 to 0.2924 mmol/g. The authors note that for all samples, the CO₂ adsorption capacity is larger than the CH₄ capacity for the same rock unit at the same pressure.
Similar to Nuttall et al. (2005), the authors also developed a relationship of the maximum CO₂ excess (gas) sorption capacity on shale, $GSC_{CO₂}$, as a function of the total organic content, $TOC$, as (Hong et al., 2016):

$$GSC_{CO₂} \text{[mmol/g]} = (0.0326 \times TOC) + 0.088 \text{ [at 14 MPa]} \quad (4)$$

Luo et al. (2015) investigated the sorption of CO₂ and CH₄ and their binary mixtures on shale samples from the Qaidam Basin, China. The samples were taken at a depth of about 2,307 m and are from the Middle-Lower Jurassic period. Samples were ground for testing and homogenized. Single component gas adsorption measurements were performed on the gas adsorption experiments setup at temperatures of 35 °C to 85 °C and at pressures up to 10 MPa. The gas adsorption capacities of powdered samples were determined as a function of pressure with the manometric method. The samples were dried prior to testing. The samples had a high clay content (72.5 to 82.5%), composed primarily of kaolinite, with some illite. The TOC of the shale was moderate, at 1 to 2%.

The isotherms for pure CO₂ sorption over a range of temperatures for the three test samples are all highly similar. The isotherms for Sample #1 are shown in Figure A18. All the isotherms exhibited a Langmuir isotherm shape, with a peak sorption occurring at 10 MPa, and a peak range from 0.293 to 0.418 mmol/g. For all the three samples, approximately a 45% reduction in the CO₂ sorption occurs over the temperature range of 35 °C to 85 °C, with sorption decreasing with increasing temperature.

For the binary mixtures of CO₂ and CH₄, (conducted at 35 °C), the series of isotherms appear roughly uniform in spacing, decreasing from pure CO₂ to pure CH₄, but favoring the higher pure CO₂ isotherm for the three samples. The series for Sample # 1 is shown in Figure A19. As noted by the authors, the results indicate that the CO₂ adsorption capacity was larger by a factor of 4 than the CH₄ on the same shale sample.

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To avoid any compositional fractionation (segregation), the sample materials were powdered to less than 0.5 mm in grain size. Sub-samples were prepared using a sample divider (homogenizer). The potential compositional changes from grinding of shale, and the potential for size fractionation were noted in other testing by Cloke et al. (2002), as mentioned by the authors.
Note:
a Results from Sample #1. Samples #2 and #3 show similar trends.

Figure A18: CO₂ Sorption on Qaidam Basin Shale at varying temperatures from Luo et al. (2015).

Note:
a Results from Sample #1. Samples #2 and #3 show similar trends.

Figure A19: Sorption of binary mixtures of CO₂-CH₄ by shale at 35 °C from Luo et al. (2015).
Charoensuppanimit et al. (2016) tested three pulverized shale samples with two samples from the Woodford Shale play (from Payne and Hancock counties) and one sample from the Caney Shale play. Samples were tested without drying at a temperature of 55.1 °C to study sorption of CO2, CH4, and N2 over a range of pressures up to 12.4 MPa. The samples had substantial organic content, with the Woodford (Payne) Shale sample with 8.49% content, Woodford (Hancock) Shale sample with 6.38%, and the Caney Shale with 2.23%. The clay mineral content of the samples was not reported.

All CO2 test results exhibited an increasing/decreasing isotherm curve with pressure as per Chareonsuppanimit et al. (2012) (e.g., Figure A11) increasing to a peak value at about 10 MPa and decreasing thereafter. The authors determined a peak CO2 adsorption capacity of 0.1616, 0.1487 and 0.1182 mmol/g for the Woodford (Payne) Shale, Woodford (Hancock) Shale the Caney Shale samples, respectively, at about 9.7 MPa. The excess adsorption also apparently exhibited a generally linear correlation with organic content (with excess absorption increasing with increasing organic content), consistent with similar observations by others. The curve fit parameters, however, were not provided.

Duan et al. (2016) tested the sorption of CO2, CH4, and mixtures of these gases on Nanchuan Shale. Tests were conducted at 5 °C, 25 °C, and 45 °C and at pressures up to 2 MPa. The Nanchuan Shale samples were from the Lower Silurian Longmaxi Formation in the southeastern Sichuan Basin. Samples were cored at a depth of 400 m below grade and were crushed and sieved prior to testing. Nanchuan Shale has an organic content of 2.6% and a clay content of 23.7%. Clay minerals include illite, kaolinite, smectite, and chlorite. Adsorption isotherms were measured using an intelligent gravimetric single gas adsorption analyzer, and experiments were performed using the static model for pure gases, while mixed gas experiments were carried out in the flowing mode.

The isotherms for pure CO2 and CH4 sorption for the three test temperatures are shown in Figure A20, together with a fitted model. All the isotherms exhibited a generally Langmuir isotherm shape, although the authors indicated that using a BET or virial model provided a better curve fit. The peak sorption values all occurred at the maximum pressure of 2 MPa, with a peak sorption range from approximately 0.09 to 0.35 mmol/g. The isotherms evidence a reduction of about 75% in the CO2 sorption over the temperature range of 5 °C to 45 °C, with sorption decreasing with increasing temperature. For the binary mixtures of CO2 and CH4, the series of isotherms appear roughly uniform in spacing, decreasing from pure CO2 to pure CH4 as for Luo et al. (2015).

103 The Woodford Shale samples were from depths of 1,300 m and 5,404 m from Payne and Hancock counties, respectively, and the Caney Shale sample was retrieved at 2,245–2,249 m below the surface.

104 Grain size range was from 1.7 to 2.3 mm.

105 For description of the virial model, see Czepirski and Jagiello (1989).
Kumar (2016) conducted CO$_2$ sorption tests on two Bakken Shale samples in both dry and water-imbibed states. Both Bakken Shale samples were described as “organic-rich” and designated by the author as BK1 and EPU119.\textsuperscript{106} BK1 had a TOC of 12.5% together with a clay mineral content of 25% (primarily illite), and a carbonate content of 10%. The EPU119 was a bitumen-extracted\textsuperscript{107} shale sample from Zargari et al. (2015) and had a somewhat lower organic content of 11%. This sample had a higher clay mineral content (34%, primarily illite), and a lower carbonate content (6%).

Before testing, both the dry and water-imbibed samples were degassed for about 24 hours under a vacuum at 150 °C. The water-imbibed samples were then pressure-saturated at 28 MPa (4,000 psi) for 48 hours. Sorption tests were conducted on the samples at a

\textbf{Notes:}
\begin{itemize}
  \item[a] Tests conducted at 5 °C, 25 °C, and 45 °C. Lines represent virial model curve fit by authors.
  \item[b] p = pressure; q = sorption.
\end{itemize}

\textbf{Figure A20: CO$_2$ and CH$_4$ sorption on Nanchuan Shale at varying temperatures from Duan et al. (2016).}

\textsuperscript{106} No detail was provided on the origin of the samples.

\textsuperscript{107} The sample was treated with toluene to remove bitumen.
temperature of 50 °C, and at pressures typically varying up to 10 MPa, but with one test (water-imbibed EPU119) was taken only to 4 MPa. The isotherms for both samples showed a constantly increasing curve with increasing pressure, with a Langmuir shape. Overall, the EPU119 samples evidenced a significantly reduced excess sorption capacity in comparison to BK1 samples, with EU119 values exhibiting only about a third of the sorption capacity of the BK1 samples. In addition, the dry sample in both cases had a significantly higher sorption capacity than the respective water-imbibed sample. In detail, the BK1 sample had a peak value of approximately 1.0 mmol/g for the dry state, and about 0.6 for the water-imbibed state. EU119 had a peak value of approximately 0.3 mmol/g in the dry state, and roughly 0.15 mmol/g for the water-imbibed state (at an equivalent maximum pressure). 108

Meray and Sinayuc (2016) 109 performed experimental adsorption measurements with CO2 and CH4 on shale samples and type BPL 110 activated carbon samples. Testing was conducted at 25 °C, 50 °C, and 75 °C, at pressures up to approximately 13.8 MPa (2,000 psia). The shale samples are from the Dadas Formation, Turkey, and have a total carbon content of approximately 4.0% and a medium clay content 111 (as described by the authors). The BPL samples were used as control tests in the program. Sorption was measured using a volumetric method. Adsorption experiments were performed on larger ground samples, 112 which were dried prior to testing.

The CO2 data from this testing shown in Figure A21 indicate an increasing sorption with increasing pressure up to a peak of about 6.5 to 9 MPa (950 psi to 1,300 psi) and followed by a moderate decrease in sorption with increasing pressure. No distinct peak is evident in these isotherms, with a maximum value of at 0.211 mmol/g at 25 °C, and about 0.10 mmol/g at 75 °C.

The authors noted that at 25 °C, the CO2 transitions from a gas to a liquid at 6.43 MPa, while at 50 °C and 75 °C, gas will transition from a gas to a supercritical fluid at about 7.38 MPa. This difference in transition pressures could explain the offset in the pressure when peak sorption occurs between the low-temperature isotherm and the other higher-temperature curves.

108 For EU119, the water-imbibed curve was extrapolated from 4 to 10 MPa to provide a more accurate comparison of values, with the excess sorption capacity at 4 MPa of only 0.1 mmol/g.

109 See also Merey (2013).

110 BPL is a granular activated carbon from Calgon Carbon Corporation, designed for use in gas phase applications. It is a bituminous coal-based product.

111 No numeric description was provided of the term, “medium”.

112 The authors state that the samples were ground and sieved to 50/85 mesh size using standard screening methods. The specific sieve standard used is not noted and the size range appears nonstandard.
Like other sorption test results, the CO\textsubscript{2} sorption on the shale was shown to be significantly higher than with CH\textsubscript{4}. The CH\textsubscript{4} sorption also did not evidence a peak with no increase/decrease in behavior. In addition, the CO\textsubscript{2} testing with the BPL samples indicated results as other authors with peak values of approximately 7.1 mmol/g with a Langmuir-shaped isotherm.

Notes:

\textsuperscript{a} 1,000 psi = 6.895 MPa.

Figure A21: CO\textsubscript{2} and CH\textsubscript{4} sorption on Dadas Shale at varying temperatures from Merey and Sinayuc (2016).
APPENDIX B: DETAILED DESCRIPTIONS OF CO₂ SWELL TESTING

B.1 SWELL TESTING SUMMARIES

B.1.1. CO₂ SWELL OF CLAY MINERALS - USING XRD METHODS

Brief summaries of relevant experimental results using XRD (and similar methods) to detect changes in clay mineral structure induced by CO₂ are discussed in this appendix. Summaries in this section include AlOtaibi et al. (2012), Giesting et al. (2012a, 2012b), de Jong et al. (2012), Ilton et al. (2012), Schaef et al. (2012), Loring et al. (2013), de Jong et al. (2014), Loring et al. (2014), and Schaef et al. (2015). The summaries focus on describing experimental conditions, sample origin and mineralogy and the results of the testing of swelling on clay minerals.¹¹³

Many of the tests described in this section used so-called “standard” clay types obtained from the Clay Minerals Society. For reference, the clay designations (including the source and type of these clay samples) were described earlier (see Table A1).

Experimental results on this topic include (in chronological order):

AlOtaibi et al. (2012) described small-scale swell testing with Na-montmorillonite and Ca-montmorillonite obtained from the University of Missouri at Columbia. Samples were separated to retain only the clay-sized fraction (i.e., less than 2 μm) and were air dried prior to testing. All tests were conducted at 25 °C with either distilled water or liquid CO₂. Tests conducted with distilled water were performed at atmospheric pressure, and tests conducted with liquid CO₂ were performed at 13.8 MPa (2,000 psi). Swell was measured on filtered clay samples collected at different times using XRD and nuclear magnetic resonance (NMR) techniques.

Results indicated that the samples subjected to distilled water alone swelled substantially after soaking 24 hours. Ca-montmorillonite samples with a basal spacing of 14.95 Å swelled 25% and Na-montmorillonite samples with a spacing of 11.67 Å swelled 60.4%. In contrast, air-dried samples soaked alone in CO₂ for 24 hours at 13.8 MPa did not swell appreciably. Samples soaked first in distilled water and then in liquid CO₂ exhibited a contraction from the state after soaking in distilled water. Ca-montmorillonite samples at a basal spacing of 18.79 Å (after water soaking) contracted 14.2% with soaking in scCO₂ and Na-montmorillonite samples with a spacing of 18.72 Å contracted 24.6%.

The authors proposed that the shrinkage was due to either: (1) replacement of some innerlayer bonded H₂O by CO₂; or (2) the diffusion of bounded H₂O into the CO₂ source.

Giesting et al. (2012a) performed small-scale swell testing with a Na-rich montmorillonite (SWy-2) obtained from the Clay Minerals Society (see Table A1). Prior to testing, the

¹¹³ The summaries are based on the cited authors’ descriptions, but include this author’s input. In addition, the summaries reflect the level of detail presented in each paper, and therefore, there is not a consistent level of discussion across the summaries. Further, the term “shale” is used here in a generic sense (in contrast to the definition provided in Lindner [2016b]), and preference is given to the author’s use of geologic terms.
samples were washed several times in distilled water and AgNO₃, cation exchanged with 1 M NaCl,¹¹⁴ and the grain size was sorted to retain clay-sized fraction (grain size less than 2 μm). Samples were then heated to temperatures of either 115 °C or 200 °C, or stored in a relative humidity of 75%. CO₂ and He were used with the prepared montmorillonite samples in tests conducted at temperatures from 22 to 47 °C and at pressures up to 64 MPa. Samples were mounted on slides in either of two high-pressure environmental chambers and examined using powder XRD techniques.

Results of the testing indicated that the amount of swelling due to CO₂ depends on the initial H₂O content of the Na-montmorillonite. The authors noted that significant expansion in the montmorillonite exposed to CO₂ occurs when the initial basal spacing values are between 10.0 and 11.5 Å; little expansion is observed below this range (0W), and no expansion is observed above it (1W), the authors note that only NaSWy₂ samples containing a mixture of the two interlayer types (0W and 1W) show expansion under the conditions studied¹¹⁵. A maximum expansion of 12.3 Å was observed in a sample with an initial basal spacing of 11.3 Å at a pressure of 5.7 MPa (for 9% swell).

Expansion due to CO₂ as a function of pressure ceased at about 5.0 MPa, with no significant expansion noted at pressures above 5 MPa up to pressures of about 64 MPa. Also, no dehydration of montmorillonite by CO₂ was observed at low H₂O contents for static exposure to CO₂. However, the authors concluded that some test results suggest that a transient pulse of CO₂ could dehydrate SWy-2. Finally, exposure to He in testing did induce limited expansion of the samples (about 2 to 3% swell), which was attributed to the expansion of the test system.

Giesting et al. (2012b) performed 9 short-term swell tests and 10 kinetics swell tests with montmorillonite (SWy-2) obtained from the Clay Minerals Society. Prior to testing, the samples were washed several times in distilled water, cation exchanged by with either 1 M potassium chloride (KCl) or 1 M calcium chloride (CaCl₂) and the grain size was sorted to retain clay-sized fraction (less than 2 μm). Samples were prepared with a range of relative humidities as they were subjected to differing heating and storage methods. Small-scale tests were conducted at temperatures from 22 °C to 25 °C and at pressures up to 4.9 MPa (as shown in author’s tables). Samples were mounted on slides in a high-pressure environmental chamber and examined using powder XRD techniques.

The results from the K-exchanged samples (K-SWy-2) behaved similarly to prior testing with Na-rich montmorillonite reported by Giesting et al. (2012a) but swelled less. Maximum expansions with K-SWy-2 samples were 12.1 Å to 12.2 Å; however, one sample had a maximum swell of 11.9 Å with an initial basal spacing of 10.3 Å at 1.1 MPa (for a 15% swell).

¹¹⁴ M = molarity = moles of solute / liters of solution.

¹¹⁵ From Giesting (2012a), the basal d₀₀₁ spacing is a function of the amount of H₂O within the interlayer spacing. From Ferrage et al. (2005), a Na-montmorillonite interlayer without any H₂O in the interlayer is at a hydration state designated 0W with a spacing of about 9.6 Å. An interlayer with only one plane of H₂O groups is noted 1W with a spacing near 12.5 Å; two planes of H₂O is denoted 2W with a spacing of approximately 15.5 Å.
swell). Again, only samples containing a mixture of the two interlayer types $0W$ and $1W^{116}$ exhibited swell.

In contrast, the Ca-exchanged samples (Ca-SWy-2) showed a different behavior. The Ca-SWy-2 samples swelled more than either similarly-exposed K-SWy-2 or Na-SWy-2 samples and exhibited no decrease at the $1W$ bound (i.e., all samples swelled). The magnitude of swelling was also apparently higher above the $1W$ bound than below (suggesting an initial water content dependence). The authors concluded that some samples suggest that the $2W$ spacing is a bound for Ca-SWy-2 as the $1W$ spacing is for the K-SWy-2 samples.

In addition, upon unloading, most samples contracted only partially. The authors surmised that the incomplete reversal was potential due to possible artifacts in the test system. Further, long-term tests by these authors also suggest that the swelling is reduced with longer exposure times.

de Jong et al. (2012) summarized the results of unconfined volumetric strain measurements on small compacted pellets of montmorillonite (SWy-1) obtained from the Clay Minerals Society. Samples were heat-treated prior to exposure to CO$_2$ and tests were conducted at a temperature of 45 °C and at CO$_2$ pressures up to 15 MPa.

Results showed that samples exhibited significant, rapid swelling at pressures up to 8 MPa but additional swelling at higher pressures ceased. The amount of swelling increased with the increasing initial basal spacing over the range of 9 to 11 Å, with a maximum swelling of approximately 2.4% occurring at a spacing of 11 Å and pressure of 15 MPa. Only minor swelling occurred with samples at an initial spacing of 9.8 Å. Swell of a shale/claystone sample was also reported (source unknown) containing 53% smectite which displayed swell volume increase approximately 1.0%, at a temperature of 45 °C and a CO$_2$ pressure of 10 MPa.

No swelling effects were observed in identical experiments performed using Argon (Ar) gas. Also, no evidence was found for CO$_2$ induced dehydration (shrinkage) of the crystal structure.

Itton et al. (2012) performed small-scale swell testing with a Na-rich montmorillonite (modified STx-1) obtained from the Clay Minerals Society. Prior to testing, the samples were cation exchanged with 1 M sodium acetate and the grain size was separated to retain only the clay-sized fraction (less than 2 μm). Suspensions of the materials were then flocculated by the addition of NaCl and subsequently placed in in the NaCl solutions. Films of the treated material were tested similarly to techniques used by Schaef et al. (2012).

Tests were conducted at 50 °C and pressures up to 9.0 MPa, with scCO$_2$ and N$_2$. Two types of experiments were performed: 1) the sample was hydrated$^{117}$ for 1 hour prior to testing with H$_2$O, then the CO$_2$ or N$_2$ was introduced; 2) the desired amounts of CO$_2$ or N$_2$ were

$^{116}$ See Ferrage et al. (2010) for hydration state spacing.

$^{117}$ Water was added to test chamber but not in contact with the sample.
mixed with H$_2$O prior to testing and then introduced to the air-dried sample. Specific solutions varied from 2% H$_2$O to supersaturated H$_2$O.

For test procedure type #1, eleven samples contracted significantly after exposure to scCO$_2$, peaking at 15% shrinkage at the point of 50% to 55% H$_2$O saturation (with an initial spacing of 19.60 Å). Two samples used in test type #2 swelled 25% to 27% after exposure to scCO$_2$, at initial saturations of 37% and 39%, and basal spacings of 12.44 and 9.90 Å, respectively.

The tests conducted with N$_2$ showed a more muted response as subjected to the test type #1 procedure. Four samples generally contracted slightly after exposure to N$_2$. The contraction peaked at 4% shrinkage at about 34% H$_2$O saturation (with an initial spacing of 15.77 Å). One test showed essentially no effect (at an initial spacing of 12.58 Å, i.e., less than $IW$), and another sample swelled slightly at an H$_2$O saturation of 95% (with an initial spacing of 19.4 Å). Of the two supersaturated H$_2$O samples, one did not contract significantly and one swelled about 5% (at spacings of 20.34 and 20.42 Å) respectively.

The authors noted that wet scCO$_2$ can dehydrate montmorillonite and induce shrinkage. In detail, the authors concluded that the partial dehydration of samples at hydration states $3W$ and $2W$ clay in this testing, when exposed to wet scCO$_2$ is of particular significance, where the transitions from the $3W$ to $2W$ and $2W$ to $1W$ hydration states each involve volume losses on the order of 15% perpendicular to the basal surfaces.

Schaef et al. (2012) conducted 12 swell tests involving scCO$_2$ and N$_2$ with a Ca-saturated dioctahedral Ca-montmorillonite (STx-1) obtained from the Clay Minerals Society. Prior to testing, samples were reacted with 1 M sodium acetate buffer at pH 5 for 2 weeks, then washed in deionized water. The grain size was sorted to retain only the clay-sized fraction (less than 2 μm). The samples were then soaked in a 5 M CaCl$_2$ solution for seven days and freeze-dried. The samples were examined using a high-pressure XRD reactor over a range of temperatures (50 °C to 100 °C) and at pressures of 9, 12.5, and 18.0 MPa. The tests examined the response of clay films using high-pressure XRD techniques.

Swell was observed in montmorillonite samples containing one water of hydration ($IW$) when exposed to anhydrous scCO$_2$ at 50 °C and 9 MPa. Similarly, swell was also noted at pressures of 12.5, and 18.0 MPa. Upon reduction applied pressure from 9 MPa, the samples returned to the initial state without apparent modification to the structure. Exposure over a range of temperature indicated only a slight contraction over the temperature range of 50 to 100 °C.

However, the testing of samples at two waters-of-hydration ($2W$) evidenced a limited contraction after pressurization, potentially indicating a partial loss of interlayer water. It was concluded that the exposure of $2W$ Ca-STx-1 to anhydrous scCO$_2$ promotes dehydration of

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118 “Wet CO$_2$” is defined by the authors as a one phase fluid dominated by CO$_2$ but containing variable amounts of dissolved H$_2$O.

119 The spacings for the hydration states for Ca- montmorillonite are defined for this paper as: $0W$ (9.55 - 9.66 Å), $IW$ (11.19 - 12.45 Å), $2W$ (15.00 - 15.50 Å), and $3W$ (18.00 - 19.1 Å) (see Monsalvo et al., 2006).
the interlayer water resulting in a negative mineral volume change that could potentially increase permeability.

In contrast to tests with scCO₂, testing of montmorillonite exposure to N₂ indicated only minor changes in the structure regardless of the initial hydration state. When exposed to water alone, the samples in the 2W hydration state expanded only slightly.

Schaef et al. (2012) concluded that contraction or expansion of the interlayer spacing of montmorillonite depends on the initial hydration state of the mineral and the presence of scCO₂. The authors note that the prevalence of montmorillonite in a specific hydration state at depth will depend on several factors including the local geothermal temperature gradient, the activity of H₂O, and differences between the geostatic and hydrostatic pressure gradient.

Loring et al. (2013) performed small-scale swell testing with a Ca-montmorillonite (STx-1) obtained from the Clay Minerals Society (see CMS, 2016b). Prior to testing, the samples were cation exchanged with 5 M CaCl₂ solution for 2 weeks and the grain size was separated to retain only the clay-sized fraction (less than 2 μm). Samples were subsequently washed in deionized water to remove excess Ca. Films of the treated material were tested similarly to techniques used by Schaef et al. (2012). Tests were conducted at 50 °C and 9.0 MPa using a combination of in situ probes, including XRD, in situ magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR), and in situ attenuated total reflection infrared spectroscopy.

The samples were first exposed to water-saturated scCO₂. Results for the Ca-montmorillonite indicated that a sample with an interlayer spacing of 14.97 Å swelled approximately 20% to a spacing of about 18.0 Å over a period of 15 hours. Subsequent exposure to anhydrous scCO₂ reduced this spacing to approximately 15.0 Å (i.e., for only a small amount of expansion from the start). From test measurements, the authors concluded that both H₂O and CO₂ are simultaneously present in the mineral interlayer during swelling. Testing was also conducted at varying H₂O concentrations in the CO₂ over a range of 0% to 40% saturation. As the H₂O concentration of the exposure solution increased, the sorption of H₂O in the clay mineral increased.

In conclusion, the authors state that extent of Ca-montmorillonite clay swelling/shrinkage is dependent not only on water hydration/dehydration, but also on CO₂ intercalation reactions, and that “…the interlayer spacing is a complex function of partitioning of water and CO₂ between the clay and the supercritical fluid.”

de Jong et al. (2014) conducted tests on sodium-exchanged Na-SWy-2 type and naturally occurring Na-rich SWy-1 montmorillonites, both obtained from the Clay Minerals Society. The sample pellets were prepared and pressed to a tile-shape of approximately 1 cm × 1 cm × 1 mm in dimension. The Na-SWy-2 sample was crushed (size-fractionated) to less than 2 μm, purified and Na-exchanged. Experiments were conducted at 45 °C on six pairs of samples of Na-rich SWy-1 characterized by six different hydration states, at CO₂ pressures up to 15 MPa. Tests were also conducted on two pairs of Na-SWy-2 under the same conditions. Deformation of each sample was recorded photographically, using digital images with a resolution of 2,088 by 1,550 pixels, representing an image of 2.3 mm by 1.7 mm (pixel size = 1.1 μm). Samples were preheated to different temperatures to achieve differing initial saturation states, with the swell tests conducted at 45 °C.
Results of tests with SWy-1 montmorillonite exposed to CO₂ indicated swell, with volumetric strain values varying from 0.55% to 2.46% (depending on the pre-drying temperature). Na-SWy-2 samples showed a similar response. Upon exposure, samples showed an immediate rapid swelling response, with most deformation taking place in just a few seconds. Samples indicated a decrease in swell magnitude with decreasing initial hydration state or basal spacing (i.e., corresponding to increasing pre-treatment temperature). The Na-SWy-2 samples showed a similar response. Swelling strain increased systematically with CO₂ pressure in the range 1 to 7 MPa but increased only slightly at higher pressures. Some recovery of strain is noted upon unloading.

In comparing the magnitude of swelling strains to earlier results, the authors suggested that lower values obtained in the present work could be due to the method of achieving the initial state. De Jong et al. established their initial state by increasing temperature, i.e., by dehydration, while others hydrated their samples by exposing them to different relative humidities. Other possible causes were also suggested.

Loring et al. (2014) conducted swell tests on Na-SWy-2 montmorillonite and KGa-1 kaolinite obtained from the Clay Minerals Society. Tests were conducted using a pressurized XRD measurement system coupled with an in-situ flow-through, transmission infrared spectroscopy capability. The clays were exposed to variably hydrated scCO₂ at 50 °C and 9 MPa.

As observed, the measured mineral innerlayer layer-to-layer spacing (d₀₀₁) increased for the clays in a stepwise fashion. Specifically, sorbed H₂O concentrations increased continuously with increasing percent H₂O saturation. The trend of the sorbed H₂O concentration increased with H₂O saturation in a bi-linear fashion, with a rate change at about a saturation of 60% (where an increased rate occurs at higher saturations). The montmorillonite samples showed significantly more response than the kaolinite ones.

Loring et al. also identify that sorbed CO₂ varies with the sorbed H₂O concentration on montmorillonite. It is noted that the results show initially a significant increase in sorbed CO₂ as the clay expands from a $0W$ to a $1W$ state, with a maximum sorbed CO₂ concentration of about 2.0 at 4 mmol/g of sorbed H₂O. The CO₂ concentration then rapidly decreases over the remainder of the $1W$ range (i.e., from 4 to 9 mmol/g of sorbed H₂O), to a value of about 1.1. The trend then transitions to a slower rate of decrease in the $2W$ range and eventually declines to roughly 0.3 at 15.8 mmol/g of sorbed H₂O.

Schaef et al. (2015) tested SWy-2 and STx-1 montmorillonites as acquired from the Clay Minerals Society. Clay samples were prepared and sorted (fractionated) to a grain size less than 2 μm following the same methods described earlier (Ilton et al., 2012; Schaef et al., 2012). SWy-2 subsamples were saturated with Ca²⁺, Na⁺, and Mg²⁺ and STx-1 with Ca²⁺ to produce homoionic samples referred to as Ca-SWy-2, Na-SWy-2, Mg-SWy-2, and Ca-STx-1, respectively. Response was investigated using in situ XRD, infrared spectroscopic titrations, and quartz crystal microbalance measurements. High-pressure titrations with infrared detection were performed at 50 °C and 9 MPa using a fully automated scCO₂ generation and delivery apparatus coupled to a high-pressure infrared cell with both transmission and attenuated total reflection infrared optics. Details of the apparatus, cell, and the method for performing titrations of clay samples are reported elsewhere (e.g., Loring et al., 2014).
Results from testing indicate changes in H₂O saturation yield step-like changes in the d₀₀₁ spacing profile for both Na-SWy-2 and Ca-SWy-2 samples. Steps reflect both swell and contraction depending on the initial d₀₀₁ spacing. The authors concluded that for Ca and Mg saturated montmorillonites, CO₂ intercalation peaks from approximately 0W to 1W equivalent hydration states, and then decreases with further hydration and with an upper limit on the capacity of clays to sequester CO₂.

In accord with previously cited experimental work (Ilton et al., 2012; Loring et al., 2013; Schaef et al., 2012; Giesting et al., 2012a), Schaef et al. (2015) concluded:

“... scCO₂ can either diffuse into or extract H₂O from the interlayer region of montmorillonites to produce volumetric changes. If the initial hydration state of the clay is low (sub 1W), yet high enough to allow interlayer access, CO₂ intercalation induces a positive volume change manifested by 0.5-0.8 Å increases in d(001). Higher hydration states (greater than 2W) presumably released some interlayer H₂O to scCO₂, and d(001) values decreased. However, when scCO₂ is oversaturated with respect to H₂O, the montmorillonite structure expands from a sub-3W to a full 3W after exposure to scCO₂ ... At this point, it is not clear whether this small expansion is caused by intercalation of CO₂ or H₂O.”

B.1.2. CO₂ SWELL OF CLAY MINERALS - LAB-SCALE EXPERIMENTS

Examples of relevant experimental results for CO₂ swell/contraction on larger samples of clay minerals (lab-scale) are discussed in this section (i.e., Heller, 2013; Heller and Zoback, 2014; Zhang et al., 2013, 2014). The summaries focus on describing experimental conditions, sample origin and mineralogy and the results of the testing of swelling on clay minerals at a lab scale (greater than 1 mm).

Experimental results with clay minerals of larger sample size include:

**Heller (2013); Heller and Zoback (2014)** conducted lab-scale triaxial swell tests on mature kerogen, kaolinite, and illite samples obtained from the Clay Minerals Society. The clay minerals were exposed to CO₂, CH₄, and He. Tests were performed on cylindrical samples, 25 mm (1 in.) in diameter and 50 mm (2.0 in.) in height at a temperature of 25 °C in a triaxial test apparatus (Figure B1). In preparation, the source material was first dried in a vacuum oven at 40 °C until constant mass was achieved. Then, the pulverized samples were placed in copper jackets and compacted by cycling the confining pressure about 15 times to a pressure 30 MPa to eliminate any recognized plastic response during loading. During each test, the sample was exposed to a series of increasing pore pressures up to a maximum pore pressure of about 9.5 MPa, while maintaining a constant differential (effective) stress of 2 MPa.

Results indicated small swelling volumetric strains for exposure to CO₂ ranging from approximately 0.03% to 0.08% with kaolinite and 0.04% to 0.17% with illite; volumetric swell with kerogen exposed to CO₂ was somewhat higher, ranging from approximately 0.03% to 0.55%. Swell deformations in tests exposed to CH₄ were, in all cases, lower than with similar test conditions with CO₂. Tests with He showed no swelling.

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¹²⁰ The specific clay type/source was not specified by authors.
Correlations of swelling deformation with sorption data on the same materials were assessed by the authors. These correlations show a definite correspondence of increasing volumetric swell with increasing sorption; in general, the correlations appear approximately linear on log-log plots. The correlations are also mineral dependent.

**Zhang et al. (2013, 2014)** conducted CO$_2$ semi-confined axial swell tests$^{121}$ using an oedometer with small compacted samples of Na-montmorillonite (SWy-1). The montmorillonite samples (15 g) were compacted into cylindrical discs with a diameter of 12 mm, and a thickness of 0.6 mm to 0.7 mm under a pressure of 60 MPa for 4 hours. Tests were conducted under initial (external) axial stresses ranging from 10 MPa to approximately 30 MPa, and at temperatures ranging from 44 °C to approximately 80 °C, at differing moisture conditions$^{122}$. Test samples were exposed to supercritical CO$_2$ under 10 MPa pressure.

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$^{121}$ It is assumed that the tests maintained a zero-volume-change over the test condition. Also, no loading paths or temperature changes during testing were noted by the authors.

$^{122}$ Specific water contents were not provided; differing initial conditions were described as “pre-equilibrated with lab air (RH = 45~55%), with liquid water at 1 bar, or under vacuum.”
The authors note that swelling stresses in the range of 5 to 11 MPa were measured, with swelling stresses decreasing with increasing initial effective stress and decreasing with increasing temperature. They also observed that higher water content samples generally developed higher swelling stresses. For control tests performed using Ar, only minor stresses (1 MPa to 2 MPa) developed with drier samples, while water-saturated samples evidenced significant stresses.\textsuperscript{123}

\subsection*{B.1.3. SWELL RESPONSE OF SHALE}

There are few reports of swell tests on mudstones with CO\textsubscript{2}. Some negative evidence can be found in the literature that no swell was observed in free swell tests such as reported by Markiewicz (2014) from tests on Polish samples, and Lahann et al. (2013) on Albany Shale (as stated by Bacon et al., 2015). The summaries here focus on describing experimental conditions, sample origin and mineralogy and the results of the testing of swelling on mudstones.

However, some swell testing on shale has been reported by Choi and Song (2012), Zhao (2015) and Lu et al. (2016):

\textbf{Choi and Song (2012)} performed a series of free-swell tests on lab-scale specimens of shale and sandstone\textsuperscript{124}. Tests were performed on cylindrical samples, 38 mm in diameter and 70 mm in height, at a temperature within the range of 80 °C to 100 °C, and at a pressure of 10 MPa. Samples were soaked in differing fluids for a period of two weeks, and the dimensions before and after were used to compute the percent swell. Specimens were immersed in five different fluids: (1) “pure” water\textsuperscript{125}; (2) brine\textsuperscript{126}; (3) scCO\textsubscript{2}; (4) a mixture of water and scCO\textsubscript{2}; and (5) a mixture of brine and scCO\textsubscript{2}.

Results of the testing are shown in Figure B2. The samples soaked in a mixture of water and scCO\textsubscript{2} swelled the most (Case “WC”), while samples immersed in the mixture of brine and scCO\textsubscript{2} (Case “BC”) swelled the least (on average). The effect of the concentration of salts in the brine reducing swell is also evident in comparing the swell of the samples immersed in water only (Case “W”) with sample immersion in brine only (Case “B”). Simply, Case “B” swelled less than Case “W”. In addition, the samples immersed in the two mixtures with scCO\textsubscript{2} show a large range in swell results, as well as the samples immersed only in scCO\textsubscript{2}.

The total amount of deformation of swell observed in these tests was very small, and in all cases, the maximum axial displacement was less than 0.12 mm (about 0.17% strain).

\vspace{1cm}

\textsuperscript{123} The authors do not provide a specific value and the text context could indicate that no significant stresses were induced.

\textsuperscript{124} Origin of rock samples were not described, and the mineralogy of the samples were not discussed.

\textsuperscript{125} The term “pure” was used by the author; it is assumed that pure water refers to distilled water.

\textsuperscript{126} The composition of the brine or other mixtures was not stated.
Zhao (2015) conducted swell tests on coals and a shale using a specially built pressure cell. The shale sample was from a deep core sample of Marcellus Shale in New York State. The core was stored under controlled temperature and humidity conditions. The test samples of Marcellus core were trimmed to small thin, tile shapes by sawing and were approximately 3 mm x 3 mm in area and less than 2 mm in thickness.

After trimming, the sample was placed on a rack in a specially-built pressure cell, and the test performed. The pressure cell was equipped with glass windows which allowed areal strain measurement before and after CO2 exposure using a high-definition microscope (Figure B3).

The test temperature was maintained at 25 °C. As a first stage, He gas was flushed into the cell several times at 0.69 MPa to displace existing atmosphere. The sample was then subjected to a pressure cycle with He gas. The test was then performed with CO2, exposing the shale to injections of CO2 at increasing pressure levels, up to 5 MPa.

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Note:

- Samples were cylindrical, 70 mm in diameter and 38 mm in height. Tests were conducted at 80 °C to 100 °C.

- Cases reflect differing saturating fluids: Case W = H2O; Case B = Brine; Case C = scCO2; Case WC = H2O + scCO2; Case BC = Brine + scCO2.

Figure B2: Shale swell varying with reaction condition from Choi and Song (2012).

127 The author provided no details on the source of the sample, or its mineral characteristics.
The results of the test are shown in Figure B4. The initial pressure step of 0.69 MPa shows a shrinkage of the sample. Thereafter, the sample expanded with gas pressure to a final gas pressure of 5 MPa. A maximum swelling strain of 0.18% was observed for the direction perpendicular to bedding. The peak strain parallel to bedding was about 0.11%.

Note: a Samples were of Marcellus Shale and were tile-shaped, approximately 3 mm x 3 mm in area and less than 2 mm thick. Tests were conducted at 25 °C.

Figure B4: Axial strain due of Marcellus Shale to CO₂ exposure by Zhao (2015).
Lu et al. (2016) conducted swell tests on mudstones at increasing, uniform pressures of CO₂. The samples were from an outcrop of the Longmaxi Formation from the Lower Silurian in the Sichuan Basin, near Yibin City, China. They had a clay content of about 15.1% and a carbonate content of 11.7%, together with small amounts of pyrite, barite, and anhydrite. The samples had a TOC of 7.9%.

Samples were cylindrical, 50 mm in diameter and 100 mm in height. Swell tests with CO₂ were conducted at five different temperatures (35 °C, 45 °C, 55 °C, 65 °C, and 75 °C) over a range of pressure, increased in stages up to approximately 15 MPa.

Tests were conducted with samples placed in pressure cells filled with CO₂ under pressure, with swell deformation recorded with axial and circumferential strain gages. The samples were oven-dried prior to testing at 80 °C for 24 hours.

The test results exhibited CO₂-induced expansion over a range of conditions. At 35 °C, volumetric strain increased with increasing pressure up to about 7 MPa and then declined with some samples (see Figure B5). However, at increased temperatures, this decline was absent (Figure B6).

![Figure B5: Volumetric swell results of Longmaxi Shale at 35 °C from Lu et al. (2016).]
Review of the Effects of CO₂ on Very-Fine-Grained Sedimentary Rock/Shale - Part III Shale Response to CO₂

Source: Lu et al. (2016)

Note:

a) Samples were cylindrical, 50 mm in diameter and 100 mm in height. Tests were conducted at 35 °C (308 K), 45 °C (318 K), 55 °C (328 K), 65 °C (338 K), and 75 °C (348 K).

b) Results from 35 °C are an average of three tests.

c) ‰ = 1/1000.

Figure B6: Volumetric swell results of Longmaxi Shale at varying temperatures from Lu et al. (2016).

The amount of expansion also was observed to decrease with increasing temperature over the range studied, with a decrease in swell deformation of approximately 40% at 75 °C from the average results at 35 °C (from 0.15% to 0.09% as shown in Figure B6). Results also show some anisotropy of the samples, with the axial deformation somewhat larger perpendicular to bedding than those parallel to bedding (Figure B7). The anisotropy was variable with pressure, and the ratio of axial to parallel deformation averaged about 1.4.

However, the overall amount of swell was small in these tests, with a maximum, volumetric swell strain of less than about 0.17%. As noted by the authors, the deformation varied with time after each load increment, and the authors identified three regions or stages. In the first region, there is an initial contraction of the sample upon the pressure increase, which lasts only a short period. The second region shows an asymptotic increase in deformation with time, eventually reaching a constant value which defines the third or final region.

For example, Sample #1 (at 35 °C and subjected to 1.98 MPa pressure) completed the first stage/region in about 2 hours and attained the third region in approximately 36 hours. These changes in deformation rates occurring after each load increment are evident in the irregular nature of deformation readings shown in Figure B7.
Review of the Effects of CO₂ on Very-Fine-Grained Sedimentary Rock/Shale - Part III Shale Response to CO₂

Notes:

a Strain results are from perpendicular and parallel to bedding on Sample #1, conducted at 35 °C (308 K).

b The sample was cylindrical, 50 mm in diameter and 100 mm in height; h = hour.

Figure B7: Axial and diametrical swell results of Longmaxi Shale from Lu et al. (2016).
APPENDIX C: DETAILED DESCRIPTIONS OF CHEMICAL REACTION TESTING

C.1 CHEMICAL REACTION TEST SUMMARIES

C.1.1. CO₂ IMMERSION / BATCH TESTING OF MUDSTONES AND CLAYS

Brief summaries of chemical experimentation with CO₂ using immersion tests or batch reaction tests are provided in this section. The experiments involve the analysis of chemical reactions due to the immersion of shale/mudstone samples in CO₂ alone or with brine within a pressure cell for extended periods of time. Efforts by Czernichowski-Lauriol et al. (1996), Kaszuba et al. (2003, 2005), Busch et al. (2009), Credoż et al. (2009), Kohler et al. (2009), Alemu et al. (2011), Carroll et al. (2011), Navarre-Sitchler et al. (2011), Liu et al. (2012), Raines (2012), Bateman et al. (2013), Carroll et al. (2013), Garrido et al. (2013), Lahann et al. (2013), Liu (2013), Wdowin et al. (2013), Wdowin et al. (2014), Tarkowski et al. (2015), Edlmann et al. (2016), Jiang et al. (2016), Mouzakis et al. (2016), Miller et al. (2016), Szabó et al. (2016), Wang et al. (2016), Yin et al. (2016) are discussed here briefly, focusing on a description of sample origin and characteristics together with the test method and test conditions. In review of this testing, the reaction cells employed are constructed of (or lined with) corrosion-resistant metals (typically gold or titanium) and use a variety of techniques to characterize the samples, including scanning electron microscopy (SEM), XRD, low-pressure nitrogen adsorption and Fourier transform infrared (FTIR) spectroscopy.

Experimental results on this topic include (in chronological order):

- **Czernichowski-Lauriol et al. (1996)** conducted 17 chemical reaction tests on several rock samples with supercritical CO₂ together with synthetic seawater or de-ionized water. The rock types included sandstone, mudstone, anhydrite, subarkose, arkosic arenite and fuller’s earth; five of the test runs involved three types of mudstones (labeled: JMP1, JMP2, JMP3). The mudstone rock units were sampled in Audlem, Staffordshire, UK, at 86.30 m to 91.86 m below grade. The units are described red-brown or brown, massive mudstone with a clay to a fine silt grade matrix consisting of very-fine-grained detrital grains, micas and illite-smectite clay with occasional dolomite grains. Mica, kaolinite, and chlorite content were also observed, but the total clay minerals content and quantities of minerals were not described. Tests were conducted for durations of 109 days (about 3 months) or 232 days (about 8 months) at a temperature of 80 °C and at a pressure of 20 MPa. For testing, a sample

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128 The summaries are based on the cited authors’ descriptions but include this author’s input. In addition, the summaries reflect the level of detail presented in each paper, and therefore, there is not a consistent level of discussion across the summaries. Further, the term “shale” is used here in a generic sense (in contrast to the definition provided in Lindner [2016b]), and preference is given to the author’s use of geologic terms.

129 The author describes the material as a mudstone from the Fuller’s Earth Formation (sic), and is characterized containing predominantly smectite (Ca-montmorillonite). Tests with this rock (numbered JMP41 and JMP42) displayed no alteration with CO₂ and left no aqueous solution after testing for analysis, and therefore, the samples are not discussed further.
(approximately 2 cm in diameter and 5 cm high) was placed in a pressure vessel, partially submerged in about 25 mL of CO₂ saturated liquid, heated to the specified temperature and then pressurized. The samples were considered dry prior to testing.

The results for the mudstone were variable:

- Test run #399 was conducted with supercritical CO₂ alone with rock type JMP1 for a duration of 8 months. After testing, the sample remained intact, and with no supercritical fluid present in the cell. The sample appeared unreacted and no secondary porosity was noted.

- Test run #373 (3-month duration, CO₂-seawater, rock type JMP1) fragmented upon removal from the cell. The upper half (unsubmerged portion) showed little change, but the lower half evidenced increased porosity. Pores were typically 10 µm in diameter and covered the lower half, which was submerged in brine. The authors concluded that the voids were created by dolomite dissolution.

- Test runs #374 and #375 were conducted for 8 months with CO₂-seawater with rock types JMP2 and JMP3 respectively. These samples evidenced increased porosity over the entire surface of the sample (but with most pitting in the lower half) and again disintegrated upon removal. In addition, both tests showed a significant liquid loss, with no fluid left in run #374. In run #374, very minor corrosion of potassium (K)-feldspar occurred in the lower portion but without secondary clay precipitates.

- Test run #376 was conducted with CO₂ and de-ionized water, for an 8-month duration with rock type JMP3. The sample also disintegrated upon removal. While the clay matrix remained unchanged, coarser K-feldspar and dolomite grains were significantly corroded and in some cases showed pitting.

The authors concluded the following:

1. The disintegration of the samples occurred (when re-hydrated with seawater or de-ionized water).
2. Significant dissolution of dolomite occurred, especially below the CO₂-fluid interface. The dissolution was limited to the external surface of the samples.
3. Minor dissolution of K-feldspar below CO₂-fluid interface was observed.
4. Possible secondary precipitation of Mg, Fe, K and aluminum silicate below the CO₂-fluid interface was observed but only for one test run with a 3-month duration (run #373).
5. The possible presence in these tests of secondary calcite following the dissolution of dolomite.
6. The observation that exposure to scCO₂ alone did not show significant alteration of the mudstone.

Kaszuba et al. (2003) tested combined arkose sample and shale specimens exposed to CO₂ under elevated temperature and pressure conditions. The arkose sample was constructed from equal amounts of naturally-occurring Minas Gerais quartz oligoclase and microcline. The shale sample was described as an argillaceous shale from the Silurian Maplewood Shale
Formation, Monroe County, NY. The sample had a significant clay content of 65%,\textsuperscript{130} composed mainly of illite,\textsuperscript{131} as well as a 27% quartz content, and the sample was crushed prior to testing.\textsuperscript{132}

The experiment was conducted within a specially designed pressure cell containing a flexible gold/titanium reaction cell. The test system was initially held at a temperature and pressure of 200 °C and 20 MPa for 1,413 hours (59 days), then injected with scCO\textsubscript{2} and allowed to react for an additional 1,924 hours (80 days). A brine was synthesized using standard laboratory-grade salts and contained Na, magnesium (Mg) and K as the predominant cations and chlorine (Cl) as the predominant anion.\textsuperscript{133} The authors state that the brine was modeled after saline aquifer compositions from the Delaware Basin of southeastern New Mexico. The rock samples were submerged in the brine, and the brine was periodically sampled and tested during the procedure.

After the scCO\textsubscript{2} exposure period\textsuperscript{134}, alteration of the shale was minor, but surfaces showed several textures and color changes indicative of fluid-rock reactions. Small cavities were also evident on the shale. In addition, patchy accumulations of halite were noted on shale surfaces.

In comparing the chemistry in the brine solution prior to scCO\textsubscript{2} injection to that at the end of the test, many of ion concentrations changed to some degree with scCO\textsubscript{2} immersion (see Figure C1 and Figure C2). Specifically, concentrations of Na and Ca ions together with boron (B) decreased slightly, about 13%; sulfate (SO\textsubscript{4}) decreased 16%, bromine (Br) decreased 18%, and aluminum (Al) decreased about 27%. In contrast, Cl increased about 15%, and K and Mg increased only about 5% and 1%, respectively. The concentration of silicone oxide (SiO\textsubscript{2}) also increased somewhat at about 7% as well as manganese (Mn) at roughly 16%. There was a major change in Fe, which increased over 640%. From measured data, it was also noted that the pH of the solution stabilized rapidly after CO\textsubscript{2} introduction and the pH value was higher for the post-introduction period (at 5.61) than prior (at 4.86).

The authors concluded that the reaction among supercritical CO\textsubscript{2}, brine, and rock exhibits relatively rapid kinetics that are similar to rates measured in systems containing little CO\textsubscript{2}.

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\textsuperscript{130} Percent by volume.
\textsuperscript{131} From Bruijn (2012), the main mineral components of Maplewood Shale are illite, phengite [mica], clinochlore [chlorite] and quartz, with (potentially) a minor amount of smectite.
\textsuperscript{132} With a grain size 5 to 15 mm in dimension.
\textsuperscript{133} At the time of CO\textsubscript{2} introduction, the brine solution contained the following: (a) Cl\textsuperscript{-} (4,612 mmol/kg); (b) SO\textsubscript{4}\textsuperscript{2-} (48.7 mmol/kg); (c) Ca\textsuperscript{2+} (20.5 mmol/kg); (d) Na\textsuperscript{+} (1,892 mmol/kg); (e) K\textsuperscript{+} (611 mmol/kg); (f) Mg\textsuperscript{2+} (1,185 mmol/kg); (g) Br\textsuperscript{-} (4.84 mmol/kg); (h) SiO\textsubscript{2} (3.32 mmol/kg); (i) Al\textsuperscript{3+} (0.18 mmol/kg); (j) Fe\textsuperscript{2+/3} (1.40 mmol/kg); (k) Mn\textsuperscript{2+} (0.099 mmol/kg); and (l) B (23.6 mmol/kg).

\textsuperscript{134} Carbonate precipitation and other aspects related to the arkose material are not discussed in this summary.
Note:

a Data from Kaszuba et al. (2003). Comparison of major ion concentrations in solution for arkose and shale specimens reacted with brine-only and brine-CO₂ for 80 days at 200 °C and 20 MPa.

b Note the difference in scales between (a) and (b).

Figure C1: Changes in major ion concentrations after testing arkose/shale from Kaszuba et al. (2003).
Kaszuba et al. (2005) tested combined arkose and shale samples exposed to CO₂ under elevated temperature and pressure conditions, in a similar fashion to Kaszuba et al. (2003). The arkose was constructed from equal amounts of naturally-occurring Minas Gerais quartz oligoclase and microcline. The shale sample was described as an argillaceous shale from the Silurian Maplewood Shale Formation, Monroe County, NY.

The sample had a significant clay mineral content (illite and mica) of 65%, together with quartz (27%), feldspar (5%), chlorite (2%, which may have included some kaolinite), together with trace quantities of pyrite. For testing, the shale sample was crushed with a maximum dimension of approximately 5 to 15 mm in dimension.

The experiment was conducted within a specially designed pressure cell containing a flexible gold/titanium reaction cell. For the primary test, the test system was initially held at a temperature and pressure of 200 °C and 20 MPa for 772 hours (32 days), then injected with scCO₂ and allowed to react for an additional 1,079 hours (45 days). A secondary test was conducted to study the interaction of brine-rock alone and was performed under the same pressure and temperature conditions for 1,845 hours (77 days) without injection of scCO₂.

The brine used in both tests was synthesized using standard laboratory-grade salts and is identical to the solution used by Kaszuba et al. (2003). As before, Na, Mg, and K were the predominant cations and Cl is the predominant anion. The rock samples were submerged in the brine, and the brine was periodically sampled and tested during the procedure.
For the brine-rock interaction alone, the Na, Cl and pH concentrations initially decreased, but appear to be generally stable after about 350 hours (about 15 days). The SiO₂ concentration increased but then stabilized after about 350 hours, and Al did not change at all. However, the remaining trace concentrations continue changing (to varying degrees) for the duration of the test. The authors suggest that this trend may be indicative of more subtle changes in the alteration mineral assemblage. In addition, no carbonate mineral precipitated in this test.

For the second part of the test (i.e., using brine-rock-scCO₂), injection of the scCO₂ produced significant changes in the brine chemistry. Specifically, major increases (more than 200%) occurred in Mg, SiO₂, Fe and Mn concentrations with Mg and Fe showing the largest increases at 415% and 8045% from just before injection to the end of the test. Concentrations of Na, Cl, and B decreased moderately (at about 13%, 6% and 15% respectively). Moderate increases were also noted with K and Ca of about 16% and 20%, respectively. No-to-little change was noted in Al, Br and SO₄ concentrations. pH, after an initial increase, remained stable for the test. The large concentration increases in some elements in this testing (especially the major changes in Mn and Mg) differ dramatically from those reported by Kaszuba et al. (2003) while the test materials and test system were highly similar.

For the brine-rock-scCO₂ testing, material changes were also observed in the rock material. Carbonate mineral precipitation was noted on surfaces. In addition, siderite was evident as euhedral crystals (about 200 to 250 μm diameter) on the shale. New magnesite crystals were also visible to the naked eye. In addition, secondary clay minerals in abundance were observed on both the arkose and the shale rock.

The authors observed that acidified brine reacted with biotite and shale to immediately enrich the brine in Mg, Fe, and Mn. Na and K concentrations, as well as steady state Cl concentrations, decreased in acidified brine. They also state that fluid-rock reaction rates are accelerated and analcime (sodium aluminum silicate) stability is enhanced in an acidified brine-scCO₂ system.

The authors concluded that the solution composition changes, as well as nucleation and growth of siderite on shale, indicate that the shale will be a reactive component in carbon sequestration and that saturation state calculations need to adapt reaction path and reactive transport models to two-phase CO₂-H₂O fluid systems.

Busch et al. (2009) performed tests of varying duration on a shale/corundum samples in a batch reactor to examine the changes in various minerals with time up to 32 days. The rock used in these experiments was the Muderong Shale Formation of Cretaceous age from Northwestern Australia (see also Busch et al., 2008). The total clay content of the sample was approximately 70%, together with 27% quartz-feldspar-pyrite and approximately 2% carbonate (siderite) content. The clay minerals are predominately illite with some smectite

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135 From readings at test times from 771 hours to 1,850 hours.
and minor amounts of kaolinite and chlorite. The samples were crushed and sieved\textsuperscript{136} prior to placement in an autoclave. Tests were conducted at five different interaction times: (1) 48 hours; (2) 142 hours; (3) 241 hours; (4) 480 hours; and (5) 768 hours. Tests were conducted at 50 °C and 15 MPa in a batch reactor. A solution of CO\textsubscript{2} and water was also placed in the reactor.\textsuperscript{137} The reaction of the rock with the solution (water) alone was not measured.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{FigureC3.png}
\caption{Changes in mineral composition after exposure to CO\textsubscript{2} - water from \textit{Busch et al. (2009)}.}
\end{figure}

Final results are shown in Figure C3. Data indicated that most changes in the minerals occurred in the period of between 142 hours and 241 hours after CO\textsubscript{2} injection and most only

\textsuperscript{136} Samples were sieved to less than 63 μm.

\textsuperscript{137} Composition of the solution was not described in detail.
changed little thereafter. The most changes occurred with the decrease in illite and the increase in smectite content. K-feldspar also increased significantly and was continuing to increase at the end of testing.

Credoz et al. (2009) conducted experiments on two mudstone samples and three clay mineral samples. One mudstone was from the Chinle Formation in Moab, Utah. The sample was collected from an outcrop and was approximately 40% mixed-layer illite/smectite, 40% quartz, 10% calcite-A, 7% hematite, and 3% calcite-B. The second mudstone is from the Comblanchien Formation in the Charmottes oilfield, within the Paris Basin, southeast of Paris, France. This sample is roughly 45% calcite, 15% mixed-layer illite/smectite, 10% kaolinite, 10% quartz, 5% gypsum, 5% pyrite, and 5% other components.

The first clay mineral sample (labeled, “Cp”) was a purified mixed-layer illite/smectite (80% to 90% illite and 10% to 20% smectite) extracted from Chinle Formation. The second sample (labeled “Fp”) was composed of smectite and mixed-layer illite/smectite from the area of Forez Province, France, and the third sample was primarily illite (label “Ip”) from the area near Le Puy-en-Velay, France.

The brine used was synthesized from standard laboratory grade salts and was a 0.25 M Na-Cl aqueous solution with a pH 6.3 (adjusted with 5 mL 0.1 M HCl in 1 L of solution). It was intended to be representative of Dogger reservoir brine from the Paris Basin.

Two types of experiments were performed with CO2, at varying temperatures (80 °C and 150 °C) and pressures (0.1 and 15 MPa) and at varying time durations (30, 45, 90, and 365 days). The first type of test utilized a dissolved CO2 in the brine solution [(aq)CO2]. The (aq)CO2 solution was prepared by bubbling CO2 gas into the brine for 2 hours to reach a pH 4.8. The second test involved injecting scCO2 into the reactor containing the sample immersed in a brine solution (which had been de-aired by circulation of Ar gas at 25° C). Reaction tests were also conducted with the brine and the material samples to examine the brine effects without CO2 (i.e., brine-only tests, or “brine+rock”).

The brine-only tests were performed on the rock samples alone and conducted at 0.1 MPa for 90 days at the two stated temperatures. These tests indicated a strong reaction of both rock samples to the synthetic brine as evidenced by substantial changes in the solutions ions and pH. The pH increased over 90 days for both rock samples, transitioning from acidic to basic, with this effect increasing somewhat at higher temperatures (i.e., 80 °C versus 150 °C).

As reported by the authors:

“For the Colorado [sic] sample, after 90 -day exposure, Ca and K concentrations increased by 20-30% at 80 °C to reach 100% at 150 °C. Na concentration only increased

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138 The modifiers -A and -B refer to the degree of Ca substitution by Fe or Mg in the mineral CaCO3; calcite-A has few substitutions, while calcite-B has about 20% of such substitutions.

139 It is assumed that the sample is in the brine during the bubbling process, but this is not clearly stated in the paper.

140 The authors consider the sample from Moab, UT as a natural analogue for geological CO2 storage in the Colorado Plateau, and hence refer to the sample as the “Colorado” sample.
at 150 °C whereas Mg concentrations strongly decreased at this temperature (a 1000-fold decrease). Si concentration revealed an inverse behavior with respect to temperature: it decreases at 80 °C and increases at 150 °C. ... In the Charmottes rock case study, the similar trends were recorded for all the major cations after 90-day of rock-brine experiments. Ca concentrations increased significantly by 50% at 80 °C and 90% at 150 °C. Na and K concentrations only increased at 150 °C. Mg concentrations again decreased strongly at 80 and 150 °C. As it was observed in Colorado case study, Si concentrations revealed distinct behaviors, decreasing at 80 °C and increasing at 150 °C.”

Al and Fe ion concentrations did not change for the brine-only tests for either rock unit.

Results for the mudstone sample from Chinle Formation from Utah are shown in Figure C4 for tests at 80 °C and in Figure C5 for tests at 150 °C. Results for the mudstone sample from Comblanchien Formation from France are shown in Figure C6 tests at 80 °C and in Figure C7 for tests at 150 °C. The brine-only reactions are substantial in these figures, and the effect increases dramatically with temperature. The trends between the two mudstones are similar at the same temperature but not identical.

Also, there is a significant change in Mg ion concentrations in these tests, with almost no Mg present under certain conditions, although there is a significant concentration in the brine alone tests. On a minor note, a small increase in concentration of Fe (0.03 mmol/L) was noted for the Chinle Formation sample with scCO₂ test at 150 °C, and for the Comblanchien Formation with (aq)CO₂ test at 80 °C (0.45 mmol/L), but no concentration of Fe is recorded elsewhere.

Results for clay mineral testing at 80 °C are shown in Figure C8. All clay samples show similar trends in ion concentration changes with differing tests.

The authors observed that the most important effect of CO₂ is the acidification of brine. In addition, XRD work revealed that the smectitisation of the mixed-layer illite/smectite at 150 °C. The destabilization of the smectite phase and the dissolution of kaolinite provided elements in solution to form a new Fe-Mg smectite:

\[
\text{Illite/Smectite (I/S) + Kaolinite \rightarrow Illitic I/S + Fe-Mg-Smectite}
\]

The authors did not observe any effects of the supercritical CO₂ on the rock samples in the 30-day experiment, but testing on clay samples showed the dissolution of the illite fraction in small amounts after 45 days at 150 °C. They also indicated that longer-term testing (i.e., greater than a year) is required to fully observe effects on the samples.
Notes:

a Data from Credoz et al. (2009) for mudstone outcrop sample from Chinle Formation, Moab, UT. All results shown conducted at 80 °C.

b Brine+Rock test conducted at 1 atm (approx. 0.1 MPa); Brine+Rock+(aq)CO$_2$ test was conducted at 0.01 MPa and Brine+Rock+scCO$_2$ was conducted at 15 MPa.

c Brine+Rock and Brine+Rock+(aq)CO$_2$ tests were exposed 90 days; Brine+Rock+scCO$_2$ was exposed 30 days.

Figure C4: Changes in trace ion concentrations with mudstone from Chinle Formation at 80 °C by Credoz et al. (2009).
Notes:

a Data from Credoz et al. (2009) for mudstone outcrop sample from Chinle Formation, Moab, UT. All results shown conducted at 150 °C.

b Brine+Rock tests conducted at 1 atm (approx. 0.1 MPa); Brine+Rock+(aq)CO₂ test was conducted at 0.01 MPa and Brine+Rock+scCO₂ was conducted at 15 MPa.

c Brine+Rock and Brine+Rock+(aq)CO₂ tests were exposed 90 days; Brine+Rock+scCO₂ was exposed 30 days.

Figure C5: Changes in trace ion concentrations with mudstone from Chinle Formation at 150 °C by Credoz et al. (2009).
Note:

- Data from Credoz et al. (2009) for mudstone outcrop sample from the Comblanchien Formation from the Paris Basin, southeast of Paris, France. All results shown conducted at 80 °C.
- Brine+Rock tests conducted at 1 atm (approx. 0.1 MPa); Brine+Rock+(aq)CO₂ test was conducted at 0.01 MPa and Brine+Rock+scCO₂ was conducted at 15 MPa.
- Brine+Rock, Brine+Rock+(aq)CO₂ and Brine+Rock+scCO₂ tests were all exposed 90 days.

Figure C6: Changes in trace ion concentrations with mudstone from Comblanchien Formation at 80 °C by Credoz et al. (2009).
Notes:

a Data from Credoz et al. (2009) for mudstone outcrop sample from the Comblanchien Formation from the Paris Basin, southeast of Paris, France. All results shown conducted at 150 °C.

b Brine+Rock tests conducted at 1 atm (approx. 0.1 MPa); Brine+Rock+(aq)CO₂ test was conducted at 0.01 MPa.

c Brine+Rock and Brine+Rock+(aq)CO₂ tests were exposed 90 days.

Figure C7: Changes in trace ion concentrations with mudstone from Comblanchien Formation at 150 °C by Credoz et al. (2009).
Shale Response to CO2

Notes:

a Data from Credoz et al. (2009) for clay mineral samples. The Brine+<Clay>^+(aq)CO2 tests were conducted at 15 MPa, conducted at 80 °C, and were exposed 45 days.

b Clay mineral samples: Cp = purified mixed-layer illite/smectite (80 to 90% illite and 10 to 20% smectite) extracted from Chinle Formation; Fp = smectite and mixed-layer illite/smectite from the area of Forez Province, France; Ip = primarily illite from the area near Le Puy-en-Velay, France.

Figure C8: Changes in trace ion concentrations with various clay mineral samples at 80 °C by Credoz et al. (2009).
Kohler et al. (2009) conducted experiments at two different scales on caprock at elevated temperature and pressure. The caprock samples were an argillite (as described by ANDRA, 2005) from the Callovo-Oxfordian Clay Formation, and taken from cores sampled at 1,560.95 m near St Martin de Bossenay, France. The rock is composed of clay minerals, calcite, dolomite associated with some Fe-rich calcite, orthoclase, and quartz with some local occurrences of gypsum, pyrite. From bulk analyses, the samples had a carbonate content of about 42% (24.8%, dolomite, 16.8% calcite) together with a clay content of approximately 40% (mixed illite-smectite 30.1%, chlorite 4.4%, kaolinite 2.8% and muscovite, 2.8%). The samples also had about 4% pyrite.

All experiments were conducted at a temperature of 150 °C, a pressure of 15 MPa, and used deionized water instead of a brine. Though not considered representative of in situ by the authors, these conditions were selected to accelerate reactions in the autoclaves and result in short test times. Pressures in this testing were controlled using N2. XRD, transmission electron microscopy and electron microprobe analyses were employed to study mineral alteration.

Two types of experiments were conducted based on specimen size. The first type (Type #1) involved powdered samples. The samples were power-sieved, enclosed in large-volume gold capsules and mixed with deionized water and solid CO2 (at -78 ºC) in varying quantities. (Some tests were performed without CO2 to provide a reference.) Samples were then pressurized and heated to the specified test temperature for the test duration of 60 days (approximately 1,440 hours). Two groups of samples with differing solid-to-solution ratios were tested in this manner.

The second type of experiments (Type #2) used cm-scale fragments, saturated with H2O, which were immersed in either H2O or CO2. This type of experiment allowed the visualization and quantification of the reactive front progress with time. For the H2O-immersion experiment, the autoclave was placed under vacuum before injection of N2. For the CO2-experiment, the autoclave was filled initially with air to atmospheric pressure to avoid water desaturation of the starting product, and then pressurized. Samples were then heated to the specified test temperature for the test duration of 30 days (approximately 720 hours).

Both types of tests show significant changes with time. Type #2 tests with the cm-scale fragments (with either H2O or CO2), show significant mineral alterations observed by surface counts. With the H2O-only experiments, changes were significant from the at-start conditions, with the carbonate content decreasing 30% while the clays, quartz and anhydrite/pyrite content increasing by 6%, 14%, and 266% respectively. With the CO2 tests, the carbonate content decreases further (17% from the water only value), and the clay minerals and quartz content increase from the water-only values by 17% and 40%

\[141\] Perhaps better described as a calcareous mudstone, based on analytical results.

\[142\] Grain size less than 20 µm.
respectively. However, the anhydrite/pyrite reverses its trend with CO2 exposure and decreases sharply by 78% (i.e., to less than 40% of original condition).

With powered samples (Type #1 testing), it is observed that the mixed illite-smectite content increases significantly in CO2 tests (in comparison to original condition). Fe-chlorite decreases significantly and the remaining clay minerals decrease slightly. The H2O-only tests of Type #1 show a similar trend but at reduced amounts.

In all tests, the reactions of inducing the illitization of clays were combined with the formation of anhydrite. These changes were accompanied by a dolomitization and a slight increase in the quartz content. The CO2-rich samples crystallized Fe2+-enriched and K+-enriched illites, whereas the CO2-free experiments precipitated Al3+-deprived and Mg2+-enriched illites.

The authors observed that in all experiments, the reactivity of the sample was surprisingly rapid. They noted, contrary to expectations, that the more significant reactivity was observed in cm-scale (fragment) samples than with the powdered samples. In addition, in comparison to modeling reaction constructs developed by the authors, the production of carbonates and secondary clays of the models were in good agreement with the detailed experimental results. However, the model for the reaction path of the H2O-only test, which ascribes the precipitation of a significant amount of kaolinite, was not observed in the experimental results.

**Alemu et al. (2011)** studied the response of two caprock types in a laboratory batch reactor, reacting the samples under various conditions with a mixture of brine and scCO2. Eight experiments were performed over a range of four different temperatures (80, 150, 200, 250 °C) and two pressures (3.95 and 11 MPa). Test durations varied from 7 to 35 days. The brine added to the reactor was 1 M NaCl, analytical grade (Merck).

Samples of two differing shales were collected from a coring in the Cretaceous Adventdalen Group (Janusfjellet subgroup) in the Central Tertiary Basin, near the town of Longyearbyen, Norway. Shale #1 (described as “carbonate-rich shale”) was sampled at a depth of 808 m and had a clay content of approximately 45% (26% illite, 19% chlorite), and carbonate content of 35% (29% calcite, 7% ankerite). Shale #2 (“clay-rich shale”) was sampled at 789 m below the surface, and had a clay fraction of approximately 60% (22% illite, 38% chlorite), together with a 5% carbonate content (siderite).

Prior to testing, samples were crushed, washed with distilled water, and then dried at 80 °C for 48 hours. At the start of each test, a mixture of rock and brine solution was placed in the reactor and then the mixture was bubbled with N2 to degasify. The system was then pressurized with CO2 (for experiments with CO2) for 24 hours and finally heated to the specific test temperature. The particles were kept in suspension by turbulent stirring at a speed of 100 rpm. No sampling was performed until the end of the experiment.

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143 The town is on Spitsbergen Island in the Svalbard archipelago, on the edge of the Arctic Ocean.

144 The samples had a final grain size of approximately 10% between 500 to 250 μm, 10% between 125 to 250 μm and 10% between 125 to 63 μm with the remainder less than 63 μm.
The changes in ion concentration with reaction time are shown in Figure C9 for Shale #1 sample when exposed to brine and scCO₂. Most ion concentrations show a relatively minor increase over the period except for the concentration of Al, which shows a steeper decrease. Testing of Shale #2 over a range of temperatures (of 80 °C to 200 °C) shows, in general, a relatively minor decrease in concentration for most ions with temperature except for K and Al (Figure C10). K ion concentration shows a gradual increase with temperature and Al has a pronounced decrease at 200 °C.

Notes:

a Tests were conducted at 11 MPa, conducted at 250 °C, and were exposed up to 35 days, with CO₂ / brine.

b The sample was from the Cretaceous Janusfjellet subgroup in the Central Tertiary Basin, Spitsbergen Island, Norway; the shale has a clay content of approximately 45% and carbonate content of 35%.

Figure C9: Change ion solution concentration with reaction time for carbon-rich shale in brine - scCO₂ from Alemu et al. (2011).
Notes:

a Data from Alemu et al. (2011) Tests were conducted at 11 MPa, and samples were exposed 21 days to scCO₂ / brine.

b The sample was from the Cretaceous Janusfjellet subgroup in the Central Tertiary Basin, Spitsbergen Island, Norway; the shale had a clay content of approximately 60% and carbonate content of 5%.

c Data point shown for K at 150 °C in figure does not agree with tabulated value in Table 4 of Alemu et al. (2011) (i.e., value shown in table is 0.89).

Figure C10: Ion concentration variation in solution with temperature for clay-rich shale in brine - scCO₂ from Alemu et al. (2011).
Testing was also conducted with Shale #2 to separate the reaction changes of shale to brine and scCO₂ exposure (“CO₂-brine”) from the effects due to exposure to brine alone (“CO₂-free”). As shown in Figure C11, ion concentrations of K, Ca and Mg are significantly less with the CO₂-brine sample than with the CO₂-free exposure. In contrast, Fe and SiO₂ ion concentrations are substantially larger with the CO₂-brine sample (together with a minor increase in Al) than for the CO₂-free exposure.

For material impacts on the carbonate-rich shale, the authors noted that the solid minerals changed extensively during the testing, with the dissolution and re-precipitation of carbonates, the dissolution of plagioclase, and the formation and dissolution of clay minerals. Both carbonates (calcite and dolomite) were partially dissolved and re-precipitated, as smaller calcite crystals with the newly formed clay minerals. Diffractogram analyses indicated that chlorite and illite were partly converted into smectite, with about two-thirds of the clays converted after 35 days.

For the clay-rich shale, examination did not find substantial mineralogical changes (in contrast to the carbonate-rich shale). No significant amount of carbonate was noted and no alteration of sample solids was detected by bulk XRD or by qualitative X-ray analysis using EDS. The only significant mineralogical alterations were the dissolution of silicate minerals.

In conclusion, the authors noted that geochemical modeling showed reasonable agreement with the experimental results, although some discrepancies existed.

Carroll et al. (2011) conducted a chemical reaction test on shale with brine and scCO₂, as part of an experimental investigation of cement reactions with rock, brine, and scCO₂.

The shale sample was from Carboniferous, Unit C10.3 cored in the Krechba Field in central Algeria. Measurements on core near the sample indicated that the unit has a high clay mineral content (about 78%) with little to no carbonate content and trace amounts of pyrite. Tests also indicated that the clay minerals were 44% illite, 30% chlorite, and 4% kaolinite.

Chemical reaction tests were conducted in gold bag autoclaves. The samples were first exposed to brine alone for 31 days and then scCO₂ was injected into the cell and the sample was exposed to the brine/scCO₂ solution for an additional 31 days. Tests were conducted at 95 °C and a pressure of 10 MPa. The brine solution used was a mixture of distilled and deionized water and various salts. Fragments of the shale were used in the tests (rather than a powdered size fraction), and samples were washed with distilled and deionized water and dried at 60 °C prior to analysis.

Changes in the reacted fluid are shown in Figure C12. As noted by the authors, the reaction of shale with brine alone (shaded area) produced rapidly-elevated levels of both Ca and Mg but which rapidly equilibrated and were steady thereafter. In addition, a very slowly increasing amount of Si was evident over the 31-day period.

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145 The synthetic Krechba brine consisted of: NaCl: 1.8 mol/kg; CalCl₂: 0.55 mol/kg; and MgCl₂: 0.1 mol/kg.
Notes:

a Data from Alemu et al. (2011) Tests were conducted at 250 °C, and samples were exposed 35 days to scCO2 / brine. The test with brine-only was conducted at 3.95 MPa, while the test with reacted with scCO2 + brine was conducted at 11 MPa.

b The sample was from the Cretaceous Janusfjellet subgroup in the Central Tertiary Basin, Spitsbergen Island, Norway; the shale had a clay content of approximately 60% and carbonate content of 5%.

c Data in the last column of Table 4 under “carbonate-rich” shale (column “B + CO2”) is in fact for “clay-rich” shale based on Table 2 and discussion in Alemu et al. (2011).

Figure C11: Changes in ion concentrations of clay-rich shale at 250 °C by Alemu et al. (2011).
Review of the Effects of CO$_2$ on Very-Fine-Grained Sedimentary Rock/Shale - Part III Shale Response to CO$_2$

Source: Carroll et al. (2011)

Notes:

a Data from shale from Salah, Algeria. Tests were conducted at 10 MPa and 95 °C; samples were first exposed to brine alone, and then scCO$_2$ was injected and reacted for 31 days.

b Shaded area (negative time) is shale response with brine-only. Symbols shown are measured values and lines are model results.

c Note: molal = mol/kg; TIC = total inorganic carbon.

Figure C12: Geochemical solution changes after scCO$_2$ exposure from Carroll et al. (2011).
With the injection of scCO\textsubscript{2}, the total inorganic carbon increased rapidly but was highly variable over the exposure period. Fe rapidly increased over the entire exposure period, and Si evidenced initially a rapid increase, which became essentially constant after 1 to 2 days. There was also a small increase in Al which faded with time. There was no significant change in Ca and Mg levels.

The authors commented that there was little apparent alteration of the shale and only small quantities of precipitates were observed on the shale surface or in the suspension. The authors also commented that the observed precipitates were possibly due to the quenching process at the end of the test.

Navarre-Sitchler et al. (2011) provided an abstract on their testing of two of the caprock samples reacted with CO\textsubscript{2} and brine. Samples were tested at 160 °C and 15 MPa for approximately 50 days. As described by the authors, SEM images showed a marked increase in pores at length scales on the order of 10 \textmu m to greater than 1 \textmu m. In some cases, precipitates were present in pore space. Dissolution features such as pitting and etching is observed on mineral grain faces.

Liu et al. (2012) conducted laboratory experiments on CO\textsubscript{2}-rock-brine interactions together with a review of relevant literature. These batch experiments involved shale exposure to a synthetic brine and CO\textsubscript{2} and were conducted within a 180 mL gold cell placed in a steel-alloy autoclave.

The samples were from the basal member of Cambrian Eau Claire Formation in the Illinois Basin. The shale samples were obtained from core sampled at depths of 1,542 m to 1,550 m in wells in Vermillion County, IN. The shale was composed primarily of quartz, orthoclase, illite, and a small amount of chlorite, but the relative compositions were not stated.

The synthetic brine contained several ion concentrations, and was prepared using reagent grade salts; the brine was modeled based on the fluid chemistry of the Mount Simon brine.

Tests were conducted with synthetic brine alone and with brine and CO\textsubscript{2} over a total period of 60 days. At the start of each test, the sample was mixed with brine only and reacted for 29 days under 30 MPa pressure at 200 °C. This period was followed by testing with added CO\textsubscript{2} for 23 days under the same conditions. Thereafter, the sample was cooled down over a period of 28 hours from 200 °C to 56 °C and then maintained at 56 °C and 30 MPa pressure for additional 7 days before test completion. The tests started with 3.7 g of the prepared shale in the presence of 130 mL synthetic brine.

Prior to testing, rock chips were crushed, dry sieved, and then ultrasonically cleaned several times using analytical grade ethanol. The solids were finally rinsed with deionized water and then freeze-dried.

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146 Abstract provided little detail. No description of the samples or the brine solution were provided.

147 The solution had the following ion concentration: Ca = 22,177 mg/L; Fe = 138 mg/L; K = 1,382 mg/L; Mg = 2,841 mg/L; Na = 49,004 mg/L; strontium (Sr) = 721 mg/L; Cl = 124,451 mg/L; Br = 523.

148 Grain size retained between 0.355 and 2 mm.
The authors only reported qualitative information on the geochemical reactions of the caprock. SEM photomicrographs and XRD analyses indicated minor corrosion of feldspar and anhydrite surfaces, together with the precipitation of secondary minerals in the samples including illite and/or smectite, and siderite near pyrite. Secondary minerals were also observed frequently bridging the pores among feldspar grains. Well-crystallized anhydrite grains were also observed with dissolution features, including pits and steps. However, as noted by the authors, these latter features may be due to the back reaction during the cooling stage of the test.

Raines (2012) tested two types of shaley caprocks over relatively short periods of time to study the geochemical effects of CO$_2$ injection into saline formations serving as reservoir seals. The two types of samples were from (1) upper portion of the Pennsylvanian, Lower Pottsville Formation; and (2) from the upper portion of the Mississippian/Pennsylvanian Parkwood Formation, both sampled from within the Black Warrior basin. The samples were taken from surface outcrops near Birmingham, AL, and both units are a mixture of illite, Fe-chlorite, kaolinite, and quartz.

Tests were conducted with specially-prepared clay mineral samples and with small (1 cm$^3$) cubes of caprock. The cube samples were cut from directly from rock samples. For clay mineral tests, rock samples were crushed, powdered, sonically disaggregated, and then centrifuged to remove the sample fraction greater than 1 μm. Some samples were subsequently subjected to a 0.1 M sodium acetate wash (to remove ions adsorbed in an exchangeable state to the clays). These washed samples were further filtered, hydrated, sonically processed, and filtered a second time. Finally, these samples were dried at 90° C for 24 hours, followed by hand grinding and storage in a desiccator prior to testing.

For batch tests, a brine solution was prepared with ultrapure (electrical resistivity = 18 MΩ-cm) water mixed with four components in the following concentrations: (1) NaCl 11.69 g/L; (2) Na$_2$CO$_3$ (sodium carbonate) = 0.53 g/L; (3) CaCl$_2$ = 1 M solution = 1.11 g/L; and (4) magnesium chloride (MgCl$_2$) 1 M solution = 0.48 g/L.

Tests were conducted at 90 °C at a calculated pressure of 10 MPa. The cubes were treated in the batch reactor with just brine or brine and supercritical CO$_2$, over a period of 159 to 167 hours (roughly 6 days). Clay samples of the units were reacted for periods of 3, 8, 12, 17, 24, 48, and 72 hours.

As stated by the author, the experimental results show (1) dissolution of illite and possible reprecipitation due to CO$_2$ exposure; (2) CO$_2$ brine induced cation exchange of K$^+$; and (3) the dissolution of silicate minerals. The author also suggests that the steady-state K/Si ratios in the data indicate quartz re-precipitation.

Test results showed that with increasing reaction time, there is a change in the composition of the clays in the powdered specimens. At time periods less than 30 hours, the results are quite variable in trend, but appear similar for both types of caprocks. Over this period, the net amount of illite decreased. However, towards the end of the test (i.e., at times greater than 149 How samples were cut, or other preparation is not discussed for cube samples.
45 hours), the relative abundance of illite increases again, suggesting the reprecipitation of the mineral. Data trends appear more consistent towards the end of the test as well.

K and Si ions, previously absent in the starting brine solution, were detected in all solutions, indicating the dissolution of reacting solids. Rapid dissolution of both Si and K were evident in each sample and most the dissolution occurred in the early portions of the experiment.

As the author notes, the SEM images showed the appearance of dissolution pits on both caprock types, and dissolution pits were also present in the sample exposed to the brine without CO2. In addition, the Pottsville Formation sample indicated a reduction in aluminosilicates and the Parkwood Formation sample showed the loss of Fe-aluminosilicate, possibly Fe-chlorite, as well as a loss of Al, K, and Fe with possible precipitation of amorphous silica.

**Bateman et al. (2013)** provided the results of long-term testing of CO2 and N2 with mudstone samples as an extension of measurements by Rochelle et al. (2006). The tests were performed in a typical batch reaction cell (Figure C13) at a temperature of 30 °C and at a pressure of 8 MPa for a duration of 43,531 hours (1,814 days, or approx. 5 years). The experiments were conducted at these conditions to compare with prior testing at the same conditions for a shorter duration of 9,383 hours (391 days or about 1.07 years).

![Batch reactor illustration from Bateman et al. (2013).](image)

**Notes:**

- PEEK = polyether ether ketone; PTFE = polytetrafluoroethylene.

The Utsira caprock was sampled at approximately 910.2 to 910.4 m below sea level in the North Sea, at about 240 km west of Stavanger, Norway for the Sleipner CO2 Storage Project. As reported by Kemp et al. (2002) for Sample #4, the rock is from the Nordland Shale Formation, which is a weakly laminated, silty mudstone with clay content dominated by illite with minor kaolinite and traces of chlorite together with variable amounts of smectite. Core analysis by Kemp et al. (2002) at 910.3 m indicated a TOC of 0.49%, a clay mineral content of approximately 50% (41.9% mica, 1.9% kaolin and 6.0% smectite, trace chlorite) and a carbonate content of 3.8%.
For testing, the rock samples were immersed in a synthetic brine, and then heated and pressurized using CO₂. The synthetic brine was developed to represent the Utsira pore water. Samples were periodically stirred. Concentration samples were periodically taken for the first 13 months, then only resampled after 5 years.

XRD analyses of the rock show that after 5-year exposure that there were only minor increases in quartz, albite, and dolomite, and no change in amphibole from the original caprock content and the final contents were approximately the same as after N₂ exposure. However, the calcite content was significantly reduced from 2.4% to less than 0.5% and the halite content, originally at 1.0%, was absent after CO₂ exposure but similar decreases were noted with N₂ exposure as well. Clay minerals amounts indicated some minor alteration (which were not shown in N₂ exposure). Mica content increased to 34.4% from 32.3%, kaolinite decreased from 7.4% to 6.9% and chlorite decreased to 1% from 2%. A small decrease in K-feldspar was also noted.

Concentration changes with time of ions in the brine solution after CO₂ exposure are shown in Figure C14 and Figure C15. From the two figures, it is evident that only three concentrations show a significant change after 9,400 hours (392 days): Fe, Al, and NO₃. In addition, some minor changes are noted for SO₄ for a period of 3,000 hours to 9,400 hours (125 days to 392 days).

The remaining concentrations remain relatively constant over the test period of 1,000 hours to 43,530 hours (42 days to 1,814 days). Not shown in these figures is a significant initial increase in the hydronium ion (H₃O) and Ca ion concentrations at less than 1,000 hours.

150 The following components were added to 8 liters of water for the synthetic brine: 206.9 g NaCl, 3.173 g KCl, 12.500 g CaCl₂·2H₂O, 42.150 g MgCl₂·6H₂O, 0.243 g SrCl₂·6H₂O, 0.007 g BaCl₂·2H₂O, 0.077 g FeCl₃·6H₂O, and 1.725 g sodium bicarbonate (NaHCO₃).

151 “Mica” is defined as undifferentiated mica species including muscovite, biotite, illite and illite/smectite, etc.

152 Rochelle et al. (2006) also shows data for B, S, cobalt (Co), Cu, Ni and Zn concentrations for the first 10,000 hours, which are not reported by Bateman, et al. (2013). For less than 10,000 hours, Cu, Ni and Zn concentrations follow a similar trend to Fe. The concentration of B is relatively constant, the trend of S is similar to SO₄, and the Co trend is variable.
Notes:

b Data from Bateman et al. (2013).

c Sample is from Nordland Shale Formation in the North Sea; the shale has a clay content of approximately 50%, a carbonate content of 3.8% and a TOC = 0.49%, based on Kemp et al. (2002).

Figure C14: Concentration changes in brine and CO₂ with time from batch reaction tests by Bateman et al. (2013) - part 1.
The authors concluded that the reactions in experiments with CO₂ were dominated by the initial carbonate mineral dissolution. They observed no definitive evidence of other changes in mineralogy (including clay mineralogy), and that the experiments showed no indication of major deleterious, geochemical reaction processes occurring with the caprock.

Carroll et al. (2013) conducted reaction tests on sandstone and shale samples with brine and scCO₂. The sandstone and shale were from core samples from the Cambrian Mount Simon Sandstone and Eau Claire Shale Formations in the Illinois Basin, near Decatur IL. Samples were taken at depths of 1,954 and 2,062 m (6,411 and 6,765 ft), and at a depth of 1,675 m (5,494 ft) for the sandstone and shale respectively. The clay minerals of the Eau Claire Shale included kaolinite and mixture of illite and smectite (a low-iron clay).

Rock fragments were placed in a gold-titanium reactor together with a synthetic brine and supercritical CO₂ at conditions of 51 °C and 19.5 MPa. CO₂ was introduced by pressurization of the rock-brine mixture in the reactor. The synthetic brine was composed of 2.1 molal NaCl, 0.2 molal KCl, 0.55 molal CaCl₂, and 0.1 molal MgCl₂. Test duration with the shale was approximately 30 days.
The authors note that the reaction of the Eau Claire Shale with brine and supercritical CO₂ yielded solution compositions that were distinct from the reaction of Mount Simon sandstone at the same conditions. At completion, the Si, Fe, and Al concentrations in the brine were about 1.5, 4, and 10 times higher¹⁵³, respectively for the shale versus the sandstone reactions. Ca and Mg concentrations were unchanged within data accuracy. The authors also observed that the Ca concentrations for the test were higher than the initial stock solution, possibly indicating evaporation.

Carroll et al. also performed geochemical modeling using published kinetic and thermodynamic constants. In comparing results to model predictions, the surrogate iron-rich clay in the model required significant adjustments to its thermodynamic constants and inclusion of incongruent reaction terms to capture the observed change in solution composition under acid CO₂ conditions. Otherwise, only modest adjustments were required to existing published constants to fit the experimental data.

**Garrido et al. (2013)** conducted batch reaction tests on crushed rock samples at elevated pressure and temperature to examine CO₂-water interactions with a porous nanostructure.

The test sample was a shale/marl from the lower unit of the Toarcian Formation, taken in an underground tunnel near Tournemire, France at depth of 131.79 m. XRD analyses showed a predominance of calcite (43%) and quartz (15.5%) together with clay minerals (mica kaolinite and chlorite)¹⁵⁴ as well as pyrite.

The pore structure was initially examined using N₂ volumetric adsorption at pressures of 0 to 1 MPa. After this characterization, the sample and synthetic brine¹⁵⁵ were introduced into a high-pressure batch reactor, and CO₂ was injected at 8.4 MPa. The test temperature was 53 °C maintained using an oil bath. The test was conducted for two months (60 days), and pore size was again characterized using N₂.

Results from N₂ adsorption/desorption testing indicated some hysteresis in the before and after CO₂ exposure isotherms with a slope change at about 50% saturation pressure. The post-test values indicated a minor increase in sorption over the entire pressure range in comparison to the pre-test trends.

In addition, comparison of the pore size distributions from before and after testing indicated an increase in pore size after testing in the range of between 0.7 ηm and 7.0 ηm. The post-test distribution also showed a new peak about 2.5 ηm with an overall shift to smaller sizes of the distribution.

Elemental changes from the 60-day exposure period are shown in Figure C16. Results evidence an increase in Ca, Mg, Na, K, Si, and HCO, with a decrease in SO₄, and Cl. No concentrations of Al were recorded. The decreases in SO₄ and the increase in HCO were the

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¹⁵³ Specific values were not listed in source.

¹⁵⁴ The clay mineral percentage was not provided. Mica was the dominant mineral. From Berthe et al. (2011), the clay content may be roughly 40% to 50%.

¹⁵⁵ Composition of the brine ("synthetic water") was not described.
most prominent. The authors note that the decrease in sulfate concentration may be indicative of possible gypsum precipitation, due to sulfate complexation with Ca released by calcite dissolution.

Lahann et al. (2013) conducted and reported tests on three shale samples at elevated temperature. The samples were taken from archived core of the (Upper Devonian-Lower Mississippian) New Albany Shale Formation of the Illinois Basin from wells in Lawrence and Sullivan Counties, IN. The three samples were designated MM1, MM3, and MM4 in the paper. Sorption data from Nuttall et al. (2005, 2009) correlates with these samples.

Samples MM1 and MM4 were both from the Clegg Creek Member of New Albany Shale with high TOC, lower clay content and a low carbonate content. Samples MM1 and MM4 had a TOC of 15.8% and 13.0% respectively. Sample MM1 had a clay content of about 40% (37% illite, 3% chlorite) with a low carbonate content (0.3%). Sample MM4 had a clay content of about 43% (39% illite, 4% chlorite) a carbonate content of about 1.0%. Samples MM1 was cored at 287 m (940 ft), and MM4 was cored at 764 m (2,506 ft) below grade.

Notes:

a Data from Garrido et al. (2013). No concentrations of Al were recorded under either pre-test and post-test conditions.

b The sample was a mudstone from the lower unit of the Toarcian Formation in France. The sample was exposed to CO₂ for 60 days at conditions of 8.4 MPa and 53 °C.

Figure C16: Changes in concentrations after exposure to CO₂-water from Garrido et al. (2013).
Sample MM3 was from the Camp Run Member and has a lower organic content, together with higher clay and carbonate contents. MM3 had a TOC of 5.8%, a total clay content of 61% (54% illite, 7% chlorite), and a carbonate content of 3.3%; Sample MM3 was sampled at 778 m (2,552 ft).

Three sets of tests were conducted with CO2. One set of experiments tests was conducted with samples MM1 and MM3 at low pressures. The samples were exposed to a brine-only solution at 0.096 MPa, and heated for periods of 4 and 21 days. A second set of tests at low pressure was performed with MM1 and MM3 to investigate the influence of adsorbed CO2 on shale mineralogy and pore structure. Samples were first enriched in CO2 at 3.8 MPa at about 15 °C, placed in a reaction chamber with water and then heated to 150 °C, for a duration of 3 to 42 days.

The third set of tests was conducted with CO2 at pressures from 0.7 MPa up to about 24.13 MPa (estimated) with samples MM1, MM3, and MM4. In this case, solid CO2 was added to the Teflon reaction chamber and the chamber was heated to 80 °C for 21 days. Variable pressures were induced within the chamber by the CO2 expansion. The internal pressure was not measured but rather was estimated from the known volumes and the equation of state for CO2.

As reported by the authors for low-pressure testing, X-ray examination with Sample MM1 showed no detectable changes in shale matrix mineralogy due to CO2 exposure, aside from an occasional orange sheen. Sample MM3, however, displayed orange-red discoloration at the base of the clay sediments. Also, XRD results indicated (possibly) smaller amounts of carbonate minerals as well, but no pattern was in evidence. The authors inferred from the discoloration that some minor oxidation of pyrite occurred during the heating phase, followed by oxidation and the formation of iron oxyhydroxide phases from atmospheric exposure after test completion.

Examining pore-related parameters, both samples indicated a small increase in surface area as a result of temperature alone. An increasing trend in mesopore volume with time was also observed. The micropore volume showed little change in these tests.

At elevated pressure, more discernable changes were indicated by the changes in the various ion concentration in brine after heating for all 3 samples. Concentrations of K ions decreased with CO2 exposure and were somewhat variable with pressure. Mg concentrations decreased at lower pressures, but then increased with pressure, and exhibited a positive at higher pressures. Ca showed increased concentrations throughout, together with an increasing trend with increased pressure. In addition, SEM examination on the sample surface of an MM3 chip showed clear evidence of etching by the CO2-rich solution at high pressures.

The authors stated that for high-pressure testing that “...while there were changes in brine chemistry and in the texture of dolomitic structures in response to the presence of CO2 at
“high pressure, no distinct changes have been observed in mesopore\textsuperscript{156} and micropore characteristics.”

From these experimental observations, authors concluded the earliest response to injection of CO\textsubscript{2} into a New Albany Shale reservoir will be carbonate dissolution, but the long-term effects are highly uncertain.

**Liu (2013)** conducted five CO\textsubscript{2} reaction tests on shale samples at moderate pressure and temperature. Tests were conducted at varying periods from 48 to 1,008 hours (2 to 42 days) at a temperature of 50 °C and a pressure of 2 MPa. A basic synthetic brine was used in testing, which was composed of a 3 g/L NaCl solution. Due to the friable nature of the samples, the pressure for the tests was kept low and shale chips were placed in special sample holders.\textsuperscript{157}

The samples used were a fissured clayey shale from the Late Cretaceous Lea Park Formation, taken at a depth of approximately 1,530 to 1,533 m in the Pembina Cardium oil field in west-central Alberta, Canada. Testing indicated that this shale\textsuperscript{158} had a total clay content of approximately 38\%, composed primarily of illite (22.0\%), chlorite (10.0\%), and kaolinite (6.0\%), together with a negligible carbonate content.

The results of the test at 1,008 hours (42 days) of exposure to CO\textsubscript{2} and brine are shown in Figure C17. Fe, N, C show increased values while K, Ca, Si, Al, and O show decreases in concentration. However, these trends were variable with time as shown in Figure C18. In the initial 400 hours of exposure, only the elements of C and O show significant changes. At approximately 400 to 550 hours, most element concentrations show a pronounced change, which remains roughly constant thereafter. However, C, O, and Si all show a more pronounced reversal in trend at 550 hours, with increasing values for Si and O and decreasing values for C from 550 hours to the end of testing.

These trends correspond somewhat to the formation and disappearance of a coating on the shale as observed by SEM observations and could be the result of the containment of the special specimen holders developed for this testing by the author.\textsuperscript{159}

\textsuperscript{156} Defined by International Union of Pure and Applied Chemistry (IUPAC), macropores have a diameter greater than 50 \(\eta\)m; mesopores have a diameter of less than 50\(\eta\)m, but greater than 2 \(\eta\)m, and micropores have a diameter of less than 2 \(\mu\)m (Rouquerol et al., 1994).

\textsuperscript{157} Specifically, sample chips were placed in an acrylic plastic sleeve and held in place with an epoxy resin to prevent sample disintegration.

\textsuperscript{158} From tests on samples from a nearby well at a depth of about 1,598 m.

\textsuperscript{159} The special sample holder may have delayed reactions of the shale with CO\textsubscript{2} for a period of time.
Notes:

a Data from Liu (2013). Tests were conducted at 50 °C and 2 MPa, and samples were exposed 1,008 hours (42 days) to CO₂ and brine.

b The sample was from the Lea Park Shale with approx. 38% clay mineral content and negligible carbonate content.

Figure C17: Changes in element concentration after long-term exposure to CO₂ from Liu (2013).
Notes:

a Data from Liu (2013). Tests were conducted at 50 °C and 2 MPa. Values show the difference in concentrations between a sample exposed to CO₂ and brine at different exposure times, relative to the concentration in the sample before testing.

b The sample was from the Lea Park Formation with an approximately 38% clay mineral content and negligible carbonate content.

Figure C18: Changes in element concentration with time after exposure to CO₂ from Liu (2013).
The author notes the following from SEM results after CO₂ exposure:

- No obvious variations are noticed within the first 48 hours.
- Clustered nodule structures (spheroid and chain-shaped) began to appear on the surface after 216 hours and at 384 hours, almost coating the entire shale surface. The chain-shaped structure had an abnormally high concentration of iron, exhibited the highest ratio of aluminum/silicon weight, and evidenced higher alteration, while the spheroid shapes were similar in chemistry to the intact shale.
- With increased exposure time, this cluster nodule coating disappeared and a new clay-like material was present on the shale surface.

The author concludes that the injection of CO₂ causes dissolution of illite and silicon with Lea Park shale and that the shale contains reactive minerals which interact with CO₂ that could affect sequestration.

Wdowin et al. (2013) and Tarkowski et al. (2015) exposed samples of sandstone, claystone, and mudstones to CO₂ for extended periods of time and assessed the impact by the SEM-EDS method. Samples were from Jurassic sandstone, claystone and mudstone units from the Zaosie anticline, near Belchatów, (central) Poland, and taken from drill core at depths between 838 and 1,436 m below grade. The samples were placed on Petri dishes in glass cylinders filled with brine and then inserted into the autoclaves for the test duration. The experiments were conducted at room temperature (20 °C to 25 °C) for 20 months at a pressure of 6 MPa. As stated by the authors, the brine solution was designed to model the composition of waters of the Zaosie anticline area.

The claystone sample (cored at 912 m) had a well-sorted grain size between 20 to 30 μm and a fabric exhibiting layering, and low porosity (with a peak size at about 4 ηm). The rock was primarily composed of quartz and micas (biotite, muscovite), as well as clay minerals (kaolinite, illite, and montmorillonite). The mudstone unit (sampled at 1,436 m) was poorly sorted in grain size, with variable laminae, differing in color, grain size and content. This unit had a higher clay mineral content, composed mainly of kaolinite and illite with smaller amounts of montmorillonite, and chlorite. (Specific percentages of the clay minerals or the total clay content was not reported for either unit.)

After testing, little change in the claystone was detected. The claystone exhibited a small amount of halite deposition, which precipitated from the brine (and which also decreased sample porosity), but there was no apparent change in mineral composition or in overall effective pore size. However, a small increase in the peak pore size at 4 ηm is noted in the plots together with a very small overall decrease in pore size elsewhere.

The mudstone sample showed an increase in pore size after the experiment over a range of 4.5 to 15 ηm, together with a more pronounced peak at a value of 4 ηm. Also, the sorption isotherm changed after testing. In addition, the chlorite was no longer apparent in the

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160 The solution contained the following: (a) Cl⁻ (741 mg/L); (b) SO₄²⁻ (396 mg/L); (c) HCO₃⁻ (195 mg/L); (d) CO₃²⁻ (334 mg/L); (e) Ca²⁺ (1.2 mg/L); (f) Na⁺ (807 mg/L); and (g) K⁺ (110 mg/L).
diffraction pattern of the mudstone and the thermogravimetric curve of the sample showed an endothermic reaction associated with the dehydration of hydroxides.

The authors noted that similar results were obtained by other authors (e.g., Fischer et al., 2010; Liu et al., 2012; Rimmelé et al., 2009; and Wollenweber et al., 2009).

Wdowin et al. (2014) subjected samples of sandstone and claystone to CO₂ for extended periods of time and assessed the impact by the SEM-EDS method. The samples were Permo-Mesozoic sedimentary rocks from boreholes in the Chabowo Anticline in the Szczecin-Mogilno-Uniejów Trough, along the north-western border of Poland. The claystones were from the Lower Jurassic, Gryfice Beds Claystone Formation at depths of 821 m (Sample #3) and 1,145 m (Sample #4) below grade. The samples were placed on Petri dishes in glass cylinders filled with a special brine and then inserted into special autoclaves for the test duration.

The experiments were conducted for 18 months at a pressure of 6 MPa. As stated by the authors, the brine solution was designed to model the composition of waters of the Chabowo region.¹⁶¹

The mineral composition of claystone Sample #3 was 37% kaolinite, 32% illite, 5% montmorillonite, and 26% quartz.¹⁶² Concentrations of pyrite, muscovite and biotite were also visible. Layering in the sample was evident with each layer having different grain size distribution. (One layer with a grain size up to 300 μm was adjacent to another layer with a grain size ranging to less than 30 μm.) Pores in this rock type are elongated with variable size and varying up to 0.8 mm in dimension.

The mineral composition of claystone Sample #4 differed slightly and was 42% kaolinite, 37% illite, and 26% quartz.¹⁶³ The structure is similar to Sample #3 as layering in the sample was evident with each layer having different grain size distribution. (One layer with a grain size up to 150 μm was adjacent to another layer with a grain size ranging to less than 30 μm.) Pores in this rock type are also elongated with variable size, and somewhat smaller, ranging up to 0.6 mm.

After testing, Sample #3 evidenced deposits of halite, mainly in the form of surface coatings on concentrations of clay minerals. Also visible were a few well-preserved concentrations of kaolinite. This sample also disintegrated (fell apart) after testing. Similarly, Sample #4 after testing evidenced deposits of halite coatings at the surface, and the coatings in locations covered a large extent of the mineral grains. Locally, euhedral halite crystals were also observed.

¹⁶¹ The solution contained the following: (a) Cl⁻ (50,700 mg/L); (b) SO₄²⁻ (728 mg/L); (c) HCO₃⁻ (110 mg L); (d) Ca²⁺ (1,178 mg/L); (e) Mg²⁺ (164 mg/L); (f) Na⁺ (29,500 mg/L); and (g) K⁺ (211 mg/L); note 1 L = dm³.

¹⁶² Calculated from XRD using Rietveld method. Percent by weight.

¹⁶³ The amount of quartz is questioned as the sum of the three mineral percentages should sum to 100% but actually sum to 105%.
Dissolution of primary minerals was shown by the increase of ions in the solution. Analysis of the final brine solution showed an increase in total dissolved solids as well as in the concentrations of Mg, Na and K ions, resulting from dissolution of the rock material (see Figure C19). (Not shown here are minor decreases of about 10% in both Na and Cl ions.) The authors also noted that the presence of halite on shale surfaces was caused by the evaporation of water from the brine solution during sampling and subsequent sample preparation, and was not a result of the experiment. It was concluded that the reactions observed in the experiment were primarily due to the supply of CO\(_2\) that dissolved in the brine, forming a weak carbonic acid and thereby reducing the pH of the fluid, which in turn reacted with the rock material.

![Figure C19: Changes in ion concentrations from testing claystones after Wdowin et al. (2014).](image)

Note: *Data from Wdowin et al. (2014). Comparison of ion concentrations in solution for claystones reacted with brine-only and brine-CO\(_2\) for 18 months at 25 °C and 6 MPa. Concentrations of Na and Cl are not shown due to concentration ranges; both ions showed a relatively small increase with CO\(_2\) exposure.*

**Edlmann et al. (2016)** conducted chemical reaction (immersion) tests on sandstone and mudstone samples from two borings as part of field-scale experimental CO\(_2\) injection study. The tested samples were from two borings (H-18 and H-2) near Heletz, Israel. Six caprock samples (Samples A to F) were taken from core in Boring H-18 over a depth range of 1,596.0 m to 1,596.47 m, and two sandstone samples were from a depth of about 1,634 m. A seventh caprock sample was taken from boring H-2 at an indeterminate depth (but shallower than the H-18 samples).

Testing of the H-18 samples indicated a moderate total clay content for the caprock samples, averaging about 32% and varying from about 24.0 to 42.1%. The clay content composed of (in decreasing order) kaolinite, illite and muscovite with lesser amounts of chlorite. The samples also had a moderate carbonate content (averaging about 8%) and lesser amounts of
anhydrite (1.4% to 3.2%) and gypsum (0% to 2.6%). The sandstone samples showed a clay content of 3.3% to 8.3%.

In comparison, the H-2 shale sample had a slightly higher clay content of 53.1%, but it was composed of the same clay minerals as in H-8 samples. The sample also had a carbonate content of about 8%, together with small amounts of anhydrite and gypsum (2.5% and 1.8% respectively). The authors also noted that the H-2 sample had a higher quartz composition and a lower plagioclase feldspar and potassium feldspar composition than the other H-18 caprock samples.

All samples were crushed prior to testing. For each sample, a brine-only reaction test and a brine with CO2 injection reaction test were conducted simultaneously. The brine used in this testing was a simple saline solution of 35,000 ppm NaCl. Both types of tests were conducted at 55 °C and ambient pressure.

Each sample was placed in a 3-arm conical flask and tested in a “static” mode (i.e., with no stirring or agitation of the samples), but with a continuous injection of CO2 gas (0.5 mL/min) to ensure a CO2-saturated brine during the entire test. Both the brine-only and the brine-CO2 reaction tests were conducted for approximately 3 months. A single sample chip was removed from each cell every week for SEM analysis. The authors referred to the overall test procedure as “cook and look.”

From the results of the caprock testing, the authors concluded:

- A decrease in calcite and dolomite was observed due to of carbonate reactivity.
- A decrease in K-feldspar and increase in illite was observed.
- A decrease in kaolinite and increase in illite was observed due to the reactivity of kaolinite.
- A high percentage of calcite was noted on one sample (H-18, Sample A). However, the remaining samples evidenced only low amounts of calcite (average of 2.3 wt%).

The chemical reactivity for sample H-2 is shown Figure C20. The data show a significant increase in illite with the injected-CO2 solution exposure, together with significant decreases in muscovite, quartz, plagioclase feldspar, and gypsum.

There are also moderate increases in K-feldspar, chlorite, and dolomite with comparable decreases in kaolinite, muscovite, ankerite, and pyrite. Overall, the shale sample shows some alteration, but it can be considered to have only minor effects on permeability.

The authors concluded that the “… bench experiments revealed that there is no significant mineral reactivity that would alter permeability in the Heletz caprock that could cause concerns during well completion and initial injection of CO2 at Heletz.”

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164 Samples were crushed into rock chips, 5 mm in average diameter.
165 Given the focus of the present study, the results of the sandstone tests are not discussed here.
Note:

a Data from Edlmann et al. (2016). Comparison of mineral weights for shale sample, Heletz H-2 as reacted with brine-only and with brine-CO$_2$ for 3 months at 55 °C and ambient pressure.

Figure C20: Mineral content changes in Heletz Shale after Edlmann et al. (2016).
Jiang et al. (2016) conducted a number of relatively short duration reaction tests of scCO₂ with shale (without brine or water). Shale samples were exposed to scCO₂ for periods of up to 5 days (120 hours) over a range of conditions. Samples were characterized before and after testing using a SEM and mercury porosimeter. Two types of tests were performed under the following conditions:

- Test Type #1 examined the surface structure and used three cylinder samples, which were treated at 50 °C, 10 MPa for 4 days. Samples were 42 mm in diameter and 10 mm in height.

- Test Type #2 examined pore structure of shale broken into fragments of about 5 mm in dimension and weighing 0.2 to 0.7 g. Three different sets of tests were performed (for a total of 18 groups with each group having 3 samples):
  a. One set of tests was conducted at a constant pressure of 8 MPa for 4 days but at differing temperatures of 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, and 90 °C.
  b. A second set was performed at a constant temperature of 40 °C for 4 days but at differing pressures of 8 MPa, 10 MPa, 12 MPa, 14 MPa, 16 MPa, and 18 MPa.
  c. The third set was performed at a temperature of 40 °C and 8 MPa but with differing durations of 0 days, 1 day, 2 days, 3 days, 4 days, or 5 days.

All samples were from the Longmaxi Formation in the Sichuan Basin, China. As reported, the samples had a TOC of 3.74%, a clay content of 42.7%, and a carbonate content of 3.16%. The specific clay minerals in the shale were not described.

From tests data, the authors made the following observations:

- With exposure, the clay minerals released crystal water and the sample grains become smaller. Organic matter was dissolved, and the primary pores and fractures were eroded, both of which enhanced connectivity.

- Mineral analyses of the shale showed that with exposure, amounts of C and Si increased and Ca, Mg and O decreased. In particular, the quantities of Si, Ca and Mg changed dramatically during testing.

- Testing indicated that the specific surface area and porosity of the shale increased with time. However, at low-pressure conditions, little effect on microstructure was observed over the temperature range of 40 °C to 90 °C.

The authors concluded that with increasing treatment time and pressure, the scCO₂ fluid increased in density and dissolving capability. As time increased, the fluid dissolved more organic matters from the pores and fractures in shale, increasing and expanding the number of shale gas seepage channels and increasing porosity.

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166 The source of the samples was not described in detail.
Mouzakis et al. (2016) and Miller et al. (2016) conducted reactive tests on mudstones from the Gothic Shale and the Marine Tuscaloosa Formations. The tests were performed with the two types of mudstones using scCO₂ and specific brines, which were developed for testing with each rock type. Experiments used both powered samples and rock fragments in the process. Tests were characterized using small angle neutron scattering combined with high-resolution SEM together with gas adsorption surface area and porosity measurements.

Four experiments (i.e., two tests for each rock type) were performed using scCO₂ and brine at conditions of 160 °C and 15 MPa, for a duration of approximately 45 days. Pressure for scCO₂ tests was maintained using CO₂. In addition, a control experiment was conducted for each rock type using only brine at the same conditions but for a shorter duration of about 35 days; Ar gas was used to maintain pressure in these tests.

The Marine Tuscaloosa sample (labeled “Marine”) is described as a Cretaceous marine shale of the Tuscaloosa Group. The unit is a silica-rich mudstone having a 19% clay content (9% chlorite, 5% kaolinite and 5% illite) with a little calcite (5%) and a TOC of about 0.73% (weight percent). The test samples were collected from a boring at 2,415 m below grade near Escatawpa, Mississippi.

The Gothic Shale Formation sample (labeled “Gothic”) is a Pennsylvanian carbonate mudstone with a high carbonate content (roughly 20% to 50%), and a TOC of between 2.2% to 4.4% (weight percent). The matrix includes illite and smectite clay minerals together with authigenic pyrite. The test samples were taken from a boring within the Greater Aneth oil field, near Aneth, Utah at 1,643 m below ground surface.

Changes in ion concentration over time for the tests are shown in Figure C21 and Figure C22. For the Marine Tuscaloosa samples reacted with scCO₂, the concentration of most constituents appears relatively stable after 400 hours except Fe, which exhibits an increasing concentration across the entire period.

SO₄ and SiO₂ show some variation at times less than 450 hours. In contrast, for the Gothic samples reacted with scCO₂, the Fe concentration shows a more erratic pattern of increase with time. Comparable to the Tuscaloosa sample, there are some early changes in SO₄ and SiO₂ and concentration of most constituents appears relatively stable after 400 hours.

From saturation state calculations, the decrease in the saturation of anhydrite (from supersaturated to saturated) over the test period for Tuscaloosa samples reacted with scCO₂ suggests the precipitation of anhydrite has occurred.

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167 The Marine Tuscaloosa brine composition with CO₂ was (in ppm): 49 SiO₂; 173 Mg; 1 x 10⁴ Ca; 7 x 10⁴ Na; 2.95 x 10³ K; 1.4 x 10⁵ Cl; 249 SO₄²⁻; 1.3 F; 3 CO₂.

168 The Gothic Shale brine composition with CO₂ was (in ppm): 56 SiO₂; 708 Mg; 1.8 Mn; 5 x 10⁴ Ca; 4 x 10³ Na; 191 K; 1.1 x 10⁵ Cl; 77 SO₄²⁻; 0.7 F; 32 CO₂.

169 Samples were ground and sieved through a 45 µm sieve.

170 The clay content estimated to be about 33% from Griffith et al. (2011).
The mudstone samples were from the silica-rich, Marine Tuscaloosa Formation.

Mudstone reacted with (1) brine alone [Marine-Brine]; and (2) scCO$_2$ and brine [Marine-CO$_2$].

Test duration was about 840 for the brine-alone test and 1,006 hours (42 days) for the scCO$_2$-brine test. All tests were conducted at 160 °C and 15 MPa.

Mineral abbreviations and symbols: Ca, calcite (open triangles); K, potassium (closed square); Mg, magnesium (inverted, closed triangles); SO$_4$, sulfate (open square); SiO$_2$, silicon dioxide (closed circle); Fe, iron (open circle).

Figure C21: Changes in concentrations during testing of Marine Tuscaloosa samples with brine and with brine-CO$_2$ after Miller et al. (2016).

Also for this test, elevated Fe concentrations are probably due to enhanced dissolution of iron-containing carbonates, and elevated silica concentrations are consistent with silicate mineral dissolution.

For the Gothic samples reacted with scCO$_2$, silica concentrations increased for the duration of the experiment, becoming significantly supersaturated.

From the analysis of SEM scans, results indicated that total porosity, pore connectivity, and surface area increased in both the brine-reacted and CO$_2$-reacted Gothic Shale samples. In contrast, with the Marine Tuscaloosa samples, the total porosity did not change significantly but the connected porosity increased in the brine-only sample, while the total porosity increased and connected porosity decreased in the CO$_2$-reacted sample.
Review of the Effects of CO₂ on Very-Fine-Grained Sedimentary Rock/Shale - Part III Shale Response to CO₂

Source: Miller et al. (2016)

Notes:

a. The mudstone samples were from the carbonate-rich, Gothic Shale Formation.
b. Mudstone reacted with (1) brine alone [Gothic-Brine]; and (2) scCO₂ and brine [Gothic-CO₂].
c. Test duration was about 840 for the brine-alone test and 1,195 hours (50 days) for scCO₂ and brine test. All tests were conducted at 160 °C and 15 MPa.
d. Mineral abbreviations and symbols: Ca, calcite (open triangles); K, potassium (closed square); Mg, magnesium (inverted, closed triangles); SO₄, sulfate (open square); SiO₂, silicon dioxide (closed circle); Fe, iron (open circle).

Figure C22: Changes in concentrations during testing of Gothic Shale samples with brine and with brine-CO₂ after Miller et al. (2016).

Mouzakis et al. (2016) concluded from this testing:

- Experimental results demonstrated that both the Gothic Shale and Marine Tuscaloosa samples experienced mineral dissolution under the simulated CO₂ sequestration conditions of the study.
- For the Gothic samples, both total porosity and connected porosity increased during testing. For the Tuscaloosa samples, total porosity increased slightly but connected porosity decreased.
- SEM images of the Gothic and Tuscaloosa samples, the CO₂-reacted samples exhibited an increased amount of and size of pores.
• The data suggest that the Tuscaloosa unit may be more susceptible to long-term degradation of sealing capacity due to geochemical reactions compared to the carbonate-rich Gothic unit.

• There was an observed decrease in connected porosity in small pores, potentially due to precipitation or clay hydration.

The authors identify the following areas for further research:

1. Evaluation of porosity changes in intact rock core under in situ pressure conditions (together with scCO₂ and brine). As such, more complicated experiments will “… shed light on the heterogeneous development of pores related to heterogeneity in fluid flow paths through the rock and spatial and temporal evolution of geochemical reactions along fluid flow paths.”

2. Additional investigations on the effect of fluid-rock ratios on batch reactions.

3. A study of reactions involving both minerals and organic matter (with CO₂), such as ion exchange, adsorption, and intercalation, which do not conform to the simplified framework of mineral dissolution and precipitation. (These reactions may obscure predicted aqueous trends and complicate interpretation of experimental data.)

4. Evaluation of the potential for mineral transformations induced by interactions between water-bearing supercritical CO₂ and shale.

In summary, it is noted that both rock units in this test program, while designated as caprocks for CO₂ sequestration, contained only minor amounts of clay minerals.

Szabó et al. (2016) conducted batch reactivity tests on three mudstones from a caprock formation from central Hungary.

The three mudstone samples were taken from different borings and depths from the Algyö Formation. Two of the borings were located near Szolnok, Hungary (borings S1 and S2) and one boring was near the town of KisÚjszállás, Hungary (boring MS1). These samples were sampled at various depths: in S1 at 1,866 m, in S2 at 2,223 m and in MS1 at 1,254 m. For simplicity, the authors labeled the samples with the same designation as the source borings (i.e., S1, S2, and MS1). Sample MS1 was considered unconsolidated, with the remaining S1 and S2 samples considered consolidated.

Although the samples were all from the same formation, some variability was observed in mineral content. The samples had moderate amounts of clay minerals (31% to 46%), which were composed primarily of illite/muscovite (25% to 32%) with little kaolinite (4% to 5%) and some chlorite in MS1 (9%) and a small amount (2%) of mixed smectite/illite in S2. The carbonate content was variable across the samples with MS1 having only a trace of carbonates, S1 with 31% and S2 with 52%. S1 and S2 were described as “carbonate-rich” units, and MS1 as “silicate” (quartz) rich.

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171 Locations approximate and estimated from small location map.
For the experimental program, two sets of tests were conducted with the samples in separate reaction cells. One set of samples (exposed to both brine and CO₂) was pressurized to about 13 MPa (12.5 to 13.5 MPa), and heated at a temperature of 180 °C. The second set of samples (exposed to brine alone) was pressurized to only 0.9 MPa to 1 MPa at 180 °C. Exposure time varied with sample type; MS1, S1, and S2 were exposed (to brine-CO₂ and to brine alone) for 32 days, 28 days and 57 days, respectively.

The brine employed in the test program was a simple saline solution of 250 mmol/L NaCl (Merck analytical grade) and was prepared using Milli-Q® water. The brine-CO₂ solution was a CO₂-saturated brine mixture. Prior to each exposure, the caprock samples were crushed and micronized. Various constituents of the brine solution were measured during testing and at the end. For testing, the samples and solution were placed in a reaction cell, first partially pressurized and then heated to the desired temperature and then finally pressurized to the desired pressure.

Geochemistry results for the test program are illustrated in Figure C23. Data indicated that the changes in ions in the brine solution with CO₂ exposure were similar but not uniform for all three samples. The authors noted that Na⁺ increased in the samples when exposed to CO₂ in comparison to the brine-only exposure for all three samples. Mg also showed an increase for all samples when exposed to CO₂. In comparison, S1 and S2 samples’ solutions showed increased levels of Fe_{total} and SiO₂, but there was no change in these ions from the MS1 solution. There was an increase in Al^{3+} in S1 and MS1 solutions but not in S2. Finally, S1 and MS1 solutions showed a decrease in Ca^{2+} but S2 indicated an increase.

Some clay alteration was observed during testing as well. From data on mineral content, the S1 and S2 samples evidenced an increase in mixed-layer illite/smectite content and an increase in smectite for S2 alone. MS1 showed a decrease in the smectite content but an increase in mixed-layer smectite/illite content. For MS1 and S2, there was also a small decrease in the illite/muscovite content. The remaining clay mineral content did not change significantly. Quartz content also decreased slightly for two samples (MS1 and S2).

The authors also provided an extended discussion on kinetic geochemical modeling results for these tests. While the agreement between model predictions and results was seen in several cases, there were areas of disagreement.

The authors noted that in all tests (with and without CO₂), the dissolution of carbonate minerals was observed and model predictions indicated feldspar dissolution. These reactions lead to secondary carbonate and clay mineral formation.

The authors concluded that the effect of CO₂ is primarily in the increase of dissolution rates of the mineral reactions.

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172 Specifically, an ultrapure water of “Type 1” as defined by various authorities (e.g., ISO 3696). It is a distilled water subjected to a purification process involving successive steps of filtration and deionization to achieve a purity characterized in terms of resistivity. Milli-Q label is a copyrighted by the EMD Millipore Corporation.

173 The resulting grain size distribution was not discussed.
Notes:

- The three mudstone samples were from the Algyö Formation.
- Test duration was 32 days, 28 days and 57 days for samples MS1, S1, and S2 respectively for both types of tests. All tests were conducted at 160 °C. The brine-only tests were conducted at 1 MPa, and the CO2-brine tests were conducted at about 13 MPa.

Figure C23: Relative composition of solutions of Algyö Formation samples after testing with and without CO2 by Szabó et al. (2016).

Wang et al. (2016): conducted tests on sandstone and mudstone samples in a basic brine solution over a period of several days. The samples were from rock units above Coal Seam #3 in the Lower Permian Shanxi Formation in the Qinshui Basin, within the Shanxi Province, southwest of Changzhi, China. In more detail, the lithic sandstone was composed of quartz, clay minerals, plagioclase and a small amount of chlorite. The calcareous mudstone was composed of clay minerals, quartz, and small amounts of K-feldspar and calcite. The clay mineral content was measured by XRD as 75% (54% illite/smectite mixed-layer minerals, 20% kaolinite, and 1% biotite) together with 23% of quartz/plagioclase/K-feldspar and 2% calcite. The field sampling method and the depth of sampling were not described.174

Experiments were conducted at a temperature of 160 °C and 15 MPa. Samples were ground to a powder175 and oven-dried at 80 °C for 48 h prior to testing. The brine (1 M NaCl solution) was added to the rock in the pressure cell and then bubbled with N2 to remove O2 from the solution. The solution and rock were then heated to the specific test temperature and

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174 It is assumed samples were taken at depth from the mine. Coal Seam #3 is approximately 830 m to more than 1,600 m below grade.

175 Pulverized to a grain size of 180 to 220 μm.
subsequently pressurized. The conditions were maintained for a period of approximately 12 days for the mudstone, but separate tests of 3, 6, 9 and 12 days duration were conducted for the sandstone. The solution was agitated to keep particles in suspension by turbulent stirring at 200 rpm.

Experiments on mudstone were conducted under two types of conditions: (1) rock suspension in a CO2-free brine; and (2) rock suspension in a brine with injected CO2 gas. All sandstone tests were conducted under Type #2 conditions (rock suspension with brine with CO2). The pressure was maintained by injecting CO2.

As shown in Figure C24, there are significant differences in concentrations after immersion in the CO2-brine solution than from the reaction with a brine-only solution. Ions of K, Fe, and Si evidenced moderate increases in concentration with CO2, which were higher by 54%, 94%, and 27%, respectively. In addition, there were substantial increases in Ca and Mg in the CO2-brine, with the increase for Ca was by a factor of about 2.4 and for Mg by a factor of 65. Moreover, the CO2-brine solution was saturated with respect to kaolinite, quartz, and smectite under the CO2-brine condition, whereas it was unsaturated with respect to these minerals under the brine-only condition. Further, for both rock types, the CO2-brine solution was unsaturated with respect to chlorite in all experiments, indicating that its dissolution would continue if the experiment was continued.

Regarding the rock sample itself, precipitation of carbonate minerals was noted on the mudstone surface. In addition, plagioclase and dolomite were detected on the mudstone by XRD and SEM.

The authors concluded from this testing, that the calcareous mudstone was more reactive than the lithic sandstone overall, as evidenced by the dissolution of calcite and illite/smectite and the formation of dolomite, siderite, illite, and chlorite. They also stated that while geochemical simulation can reflect the dissolution and precipitation state of minerals to some extent, but it did not entirely coincide with the observed experimental results.
Yin et al. (2016) studied the scCO2 reactions (without brine or water) with two types of samples to assess the effect on shale structure. The shale samples were from Longmaxi Formation in the Fuling (FL) and in Changning (CN) regions in the Sichuan Basin, east and southwest (respectively) of Chongqing, China. The CN samples were taken from an outcrop and had an average TOC of 4% and a clay content averaging about 30% (with illite, kaolinite, montmorillonite, and chlorite)\textsuperscript{176} together with a carbonate content of about 15%. FL samples were from core and had somewhat lower organic and clay content, with a TOC averaging 3%, a total clay content of about 26% and a carbonate content of about 12%.

The shales were inserted into a pressure cell and then exposed to scCO2 for 30 days at a nominal temperature of 40 °C and at pressure 16 MPa. Samples were characterized before and after exposure to scCO2. The characterization methods included SEM, XRD, and low-pressure nitrogen adsorption FTIR spectroscopy. Sample preparation included the pulverization of samples\textsuperscript{177} but otherwise, the preparation method was not described in detail.

\textsuperscript{176} Specific percentages of the mineral constituents were not provided by the authors.

\textsuperscript{177} Samples were crushed to a particle size of 125 to 150 μm.
In summary, the authors observed similar effects on both shales including the following:

- Experimental evidence indicated that organic matter and mineral components were reduced due to the dissolution by exposure to scCO₂.

- In most cases, scCO₂ interactions show a small decrease in average pore volume (see Figure C25) and a small increase in average pore width. However, the interactions did not change the average pore shape of shale. Importantly, the interactions had more of an effect on micropores rather than on the meso- and macropores of the samples (Figure C26). After exposure, the specific surface area, the total pore volume and the number of micropores of the samples decreased significantly, while the average pore width (across the range of pores) increased.

- After exposure, the fractal dimensions of the shale pore structure decreased, suggesting a decrease in the degree of roughness of the geometrical surface, and the morphology of the shale pore structure transformed gradually from complex to regular.

- N₂ adsorption-desorption isotherms of both shale samples indicated that scCO₂ exposure significantly decreased N₂ sorption. The authors concluded that as scCO₂ dissolves a portion of the organic matter in shale, the number of micro- and mesopores decrease, thus decreasing the adsorption capacity of the overall sample.

- N₂ adsorption-desorption isotherms also exhibited significant hysteresis above 0.4 relative pressure (relative to the saturation vapor pressure).

The authors identified two possible processes that could explain the changes in pore structure: (1) the dissolution effect of scCO₂ (especially on organic matter), which enlarged the pore size, and (2) the CO₂ adsorption-induced swelling, which narrowed the pores. Either process could affect the flow of CO₂ flow through the rock pore system.

178 Macropores are defined as having diameter greater than 50 nm; mesopores are defined with a diameter of less than 50 nm, but greater than 2 nm and micropores are defined as having a diameter less than 2 μm (Rouquerol, et al., 1994).
Shale reacted with scCO₂ (only) for 30 days (720 hours) at 40 °C and 16 MPa.

The shale samples were from the Longmaxi Formation in the Fuling (FL-1 and FL-2) and in the Changning (CN-1 and CN-2) regions of the Sichuan Basin, south-central China.

**Figure C25:** Change in the average pore volume of shale samples before and after scCO₂ exposure from Yin et al. (2016).

Shale reacted with scCO₂ (only) for 30 days (720 hours) at 40 °C and 16 MPa.

**Figure C26:** Change in micropore volume before and after scCO₂ exposure from Yin et al. (2016).
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APPENDIX D: DETAILED DESCRIPTIONS OF CO₂ FLOW TESTING

D.1. GENERAL

This appendix briefly summarizes the experimental results of current permeability testing with CO₂ flow through rock and rock fractures. Although, permeability testing of geomaterials is a standard method in the industry, the aspect that the influx of CO₂ reacts with a rock material such as shale introduces complexity not evident with water or non-reactive gas permeability alone. The introduction of CO₂ (or mixtures of CO₂ and brine) alter the flow characteristics of the host material with time, changing permeability, porosity, and wettability (Müller, 2011). This reactivity and time-dependent characteristic must be considered in examining all laboratory test results with CO₂ and shale.

The reactivity must also be considered in experimental design, as corrosion will affect results and destroy equipment. A recent review of laboratory core flooding methods was conducted by Sun et al. (2016) and provides an overview of the test systems and range of conditions as applicable to sequestration. The paper provides an overview of mechanisms of CO₂ trapping and a summary of experimental papers with a focus on the testing on sandstones. In addition, the authors identify potential areas of future research, including:

- Develop methods for the real-time dynamic monitoring of a migrating CO₂ front within a rock specimen.
- Develop new test cells to resist corrosion and provide long operational life at elevated temperature and pressure conditions.
- Develop advanced measuring devices, such as optical fiber sensors, that are resistant to electromagnetic interference and corrosion. The authors note that traditional instruments such as strain gages and electrical sensors are insufficient to satisfy current test requirements.
- Conduct additional testing of fluid and rock samples from different locations and at differing times to evaluate the spatial variation of the pore fluids and the host rock response to CO₂ and how these aspects change with time.
- Improve field techniques to investigate the fate of the injected CO₂ reservoir, to monitor the multiphase flow of CO₂ and brine, to evaluate the effects of stress on permeability, and to assess the dissolution and chemical interaction of the CO₂ with the rock minerals.
- Improve specifications for multiphase flow tests as there is a general lack of a set of appropriate specifications from experimental preparation to final interpretation.
D.2. CO₂ FLOW TESTING SUMMARIES

D.2.1. EFFECTS OF CO₂ GAS FLOW THROUGH INTACT SAMPLES

Given the low permeability of shale and mudstones in general, permeability testing is frequently performed using gas versus a (supercritical) liquid to reduce test times (i.e., gas is less viscous than a fluid). He gas is often used in permeability testing as this gas evidences little reaction with mudstones as well as the convenience and availability of this gas for testing.

A review of experimental work on the gas transport in shales was conducted by Gensterblum et al. (2015). The authors provide a description of the various transport mechanisms and applied experimental methods used for low permeability determinations of mudstones, which include descriptions of aspects such as single and multiphase flow and slip flow. Unfortunately, the results surveyed involve gases such as He, Ar, N₂, and CH₄, and lack a description of reactive processes that can influence transport such as with CO₂. However, there are several important observations of a general nature in this paper. A compilation of results by the authors show for mudstones that the ratio of permeability parallel to bedding \( (k_h) \) to that perpendicular to bedding \( (k_v) \) with (non-reactive) gases can vary widely, with ratios of \( (k_h/k_v) \) ranging from \( 10^{-1} \) to \( 10^{+6} \), with typical values much greater than 1.0. The authors also note that low permeability rock such as mudstone is characterized by small pore sizes (ranging down to the \( \eta \)m), which results in higher capillary resistance, and lower relative non-wetting phase permeability.

A limited number of experimental studies have been conducted with CO₂ gas to study the reactive behavior on permeability. Results from Miller et al. (1980), Wollenweber et al. (2009), Elsworth et al. (2012), Amann-Hildenbrand et al. (2013), Al Ismail et al. (2014), Guo (2014), Kumar (2014), and Kumar et al. (2016) on this topic are summarized in this section.¹⁷⁹

Significant findings from these researchers include:

**Miller et al. (1980)** conducted various laboratory investigations to study the effects of an aqueous CO₂ solution, water and a proprietary drilling foam on shale samples. The shale samples were taken from Devonian core samples obtained from various wells in the eastern U.S. All test specimens are stored in desiccators after being cut from core.

Pulse-decay permeability tests were conducted on small (25 mm height x 25 mm diameter) samples using He gas before and after various treatments. Tests were performed at about 17 °C to 20 °C, at pore (gas) pressures up to 7 MPa¹⁸⁰. Treatment of the samples evidenced various changes in permeability response.

¹⁷⁹ The summaries are based on the cited authors’ descriptions but include this author’s input. In addition, the summaries reflect the level of detail presented in each paper, and therefore, there is not a consistent level of discussion across the summaries. Further, the term “shale” is used here in a generic sense (in contrast to the definition provided in Lindner [2016b]), and preference is given to the author’s use of geologic terms.

¹⁸⁰ The maximum flow (gas) pressure was always maintained at 0.7 MPa (100 psi) less than the applied confining pressure.
In their report, the following aspects were noted:

- Permeability with He of untreated samples at a confining pressure of about 5.3 MPa was observed to increase with increasing fluid pressure, and permeabilities were approximately the same when the flow direction was reversed. Permeability values were also observed to decrease exponentially with confining pressure. Repeated tests on one sample obtained essentially identical results within experimental error. For untreated samples, permeabilities were in the range of 20 mD to about 5,000 mD.

- Vacuum drying of one specimen apparently increased the permeability by a factor of 3, increasing the He permeability roughly from about 200 mD before treatment to about 600 mD afterward at an applied fluid pressure of 4.1 MPa.

- Testing of a specimen treated by immersion in a solution of water with 33% CO$_2$ for 25 minutes at 4.7 MPa showed that the permeability with He decreased by about 75% immediately afterward at a 5.3 MPa confining pressure. However, the He permeability of the sample increased with time and eventually recovered to the initial value at about 140 hours.

- Treatment of samples by immersion in water with 33% CO$_2$ for 4 hours at 5.5 MPa resulted in one case with no permeability detected at 6.2 MPa applied pressure$^{181}$, and in another case with about a 50% reduction in He permeability immediately after treatment. The permeability with He continued to decrease with time at 3.3 MPa applied pressure and decreased to a value of approximately 1 $\eta$D at 90 hours after treatment.

- Treatment of samples with 33% CO$_2$ for 64 hours at 4.1 to 4.6 MPa induced a two-orders of magnitude reduction in permeability with He immediately after treatment (to about 3.3 mD at 3.4 MPa applied pressure). The permeability of the sample, however, increased somewhat with time to about 9 mD after 210 hours.

- Treatment of samples with water for two hours at 4.8 MPa applied pressure decreased the permeability from about 50 mD at 3.4 MPa applied pressure to about 6 mD. This reduced permeability showed little change with time. Subsequent treatment with a vacuum for 96 hours increased the permeability to about 100 to 400 mD.

- Tests were also conducted with kerosene and foamed fluid, which also indicated time-variant permeability results after treatment.

- Extended-term leaching experiments (eight days) were conducted with aqueous CO$_2$ at 40 °C, and at 9.0 to 11.7 MPa. The results indicated that the final solutions from the aqueous CO$_2$ treatments consisted principally of Ca and other alkaline earth and iron compounds, whereas water solutions were primarily alkali metal (Na, K) compounds.

$^{181}$ Applied pressure is in this context the pressure change of He gas across the sample for the permeability test.
Wollenweber et al. (2009) performed single-phase permeability measurements, gas breakthrough experiments and diffusion tests with He and CO2.

For this study, two samples were selected at different depths from the Upper Cretaceous sequence of Muensterland Basin in western Germany. The first sample was a gray marlstone from the Emscher Marl Formation, cored at 128 m depth below grade (Sample #05-960). The unit had a calcite content of approximately 40% together with a moderate clay content dominated by smectite and a minor amount of kaolinite. The second sample was a blue-colored limestone from a depth of 813 m. The sample was primarily calcite (about 90%) with a trace of anhydrite.

Flow properties were determined on cylindrical plugs, either 28.5 or 38 mm in diameter and between 10 and 20 mm in height. The samples were tested at temperatures of 21 °C to 45 °C. Permeability tests were conducted at confining pressures of up to 50 MPa, with the confining pressure always at least 10 MPa greater than applied fluid pressures. The breakout tests were conducted at room temperature for periods up to 150 hours. Diffusion tests were performed at 45 °C with durations up to 240 hours.

For the test sequence on each sample, single-phase permeability with water was determined first, followed by series of the CO2 gas breakthrough tests with each followed by a permeability test with water, and finally, several diffusion tests were conducted. The single-phase flow experiment was performed with tap water.

For the marlstone, the single-phase permeability tests indicated a substantial increase in sample permeability after the first successful gas breakout test with CO2 (the first two sequences using He failed) with permeability increasing from about 32 to 34 \( \eta D \) to 40 to 43 \( \eta D \), and remaining roughly constant thereafter. The alternating CO2 breakthrough pressures in this testing decreased with each breakthrough test, decreasing from 0.64 MPa to 0.43 MPa (for the three tests with CO2), and the effective maximum permeability increasing from 1.0 \( \eta D \) to 2.9 \( \eta D \). The single successful He breakthrough tests (performed after the first CO2 breakthrough test) indicated a breakthrough pressure of 0.44 MPa and an effective maximum permeability of 4.0 \( \eta D \).

The subsequent diffusion testing with the marlstone sample yielded an effective diffusion coefficient of 7.8 x 10^{-11} m²/s; a second diffusion tests yielded an increased value of 1.2 x 10^{-10} m²/s.

At the two major stages of the test program, X-ray diffraction measurements indicated that CO2 exposure affected the mineral composition of the marlstone sample. After breakthrough testing and permeability testing, the sample showed a small decrease in smectite content, and the elimination of the kaolinite content, together with a small increase in calcite. After the CO2 diffusion tests, the calcite evidenced a pronounced increase (from 40.1 vol% to 56 vol%) and anorthite decreased significantly in the sample (from 13.9 vol% to 1.1 vol%);

\(^{182}\) The focus of this review is on shales/mudstones, and therefore, the test results with other rock types are not discussed.
minor increases in orthoclase and smectite and minor decreases in muscovite and magnesite were also observed at this point.

The authors concluded that experimental study indicated significant changes in the fluid transport properties upon successive treatment with CO$_2$. These changes were likely to be due to mineral alterations and/or changes in the mineral texture due to dissolution and precipitation of minerals (carbonates). Repetitive CO$_2$ treatment resulted in a reduction of the capillary sealing efficiency and, in consequence, in an easier and faster propagation of the non-wetting fluid into/across caprocks.

Elsworth et al. (2012) briefly presented permeability tests results from two tests using CO$_2$ and He. The samples are described as porous shales and each is first tested with He, then CO$_2$ and then finally again (reswept) with He. Sample #1 was conducted at a confining stress of 10 MPa, and Sample #2 at a confining stress of 12 MPa. Gas pressures ranged from about 1 to 6 MPa. Test temperature, sample orientation and other details on the test method are not reported.

Results from the tests are shown in Figure D1. The CO$_2$ permeability results are lower than with He, and CO$_2$ results decrease with increasing gas pressure. In addition, the last stage test (i.e., when reswept with He) indicates that the flow system has been altered by the CO$_2$ exposure to some extent in both samples, as the second He permeability shows a decrease from the first measurement.

Amann-Hildenbrand et al. (2013) evaluated fluid flow properties of several rock types using permeability and gas breakthrough tests under elevated temperature and pressure conditions. In particular, the authors tested the gas breakthrough pressure of CO$_2$ and He with three groups of mudstones.

The first group of samples was obtained from the ZeroGen Northern Denison Trough storage site in eastern Australia. The shale/siltstone units had a moderate clay content, predominately composed of illite and smectite (including mixtures), ranging from 34% to 44%, with minor amounts of kaolinite and chlorite (2% to 5%). The units also had a generally low but variable carbonate content of about 2% to 15%. In addition, the units had minor amounts of pyrite, anhydrite and gypsum, and a TOC of 1.4% to 4.2%.

The second group was described as an overconsolidated shale of the Opalinus Clay Formation from the Mont Terri Underground Research Laboratory near St. Ursanne, Switzerland. The unit was stated as having a clay mineral content of about 60%, which was predominately illite-smectite with minor kaolinite and chlorite. The carbonate content was around 9% together with traces of pyrite and gypsum detected.

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183 The duration of CO$_2$ exposure was not noted by authors.
184 The unit is often described as a mudstone rather than a clay (e.g., Delage et al., 2010), as it has an average unconfined compressive strength of roughly 7 MPa (e.g., Amann F. et al., 2011).
The third group of samples was from the Boom Clay Formation\textsuperscript{185} at the High Activity Disposal Experimental Site (HADES), Underground Research Laboratory in Mol, Belgium. The unit typically has a clay mineral content ranging from 43 to 59\%, also dominated by illite and smectite (including mixtures).\textsuperscript{186} The carbonate content of the unit was typically very low (less than 1\%), and the unit contains traces of pyrite, sulfate, and gypsum.

Fluid flow properties were determined on cylindrical plugs, either 28.5 mm or 38 mm in diameter and between 10 and 20 mm in height. The samples were tested at temperatures of

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\textsuperscript{185} The unit is a weak mudstone and is often described as a stiff clay, having unconfined compressive strength of only about 2 MPa (e.g., Delage et al., 2010).

\textsuperscript{186} Other references indicate that the unit has only a small smectite content and often the clay mineral content dominated by kaolinite (e.g., Deng et al., 2011).
20 °C to 45 °C and at confining pressures of 15 MPa to 30 MPa. For each breakthrough test sequence, permeability with water was determined first, followed by a gas breakthrough test, and then finally, the samples were re-saturated with water. The single-phase flow experiment was performed with a CO2-saturated brine (10 g NaCl/L); a brine permeability test was conducted prior to using the CO2 saturated brine.

Four gas breakthrough experiments and one single-phase permeability test were performed with mudstones. CO2 breakthrough experiments were conducted using group #1 and group #3 mudstones, and the single-phase permeability was evaluated with a group #1 mudstone.

Two of CO2 breakthrough experiments apparently did not yield a permeability value but rather produced flows from diffusion through the sample. For the remaining two samples, a breakthrough occurred between 5 and 13 MPa (CO2, confining stress equal to 21 MPa to 26 MPa), and the imbibition snap-off pressures were 3.3 MPa with CO2.

For the single-phase flow experiment, (conditions: 8 to 20 MPa, 35 °C), an initial permeability for the brine-only flow was determined to be about of $2 \times 10^{-22}$ m$^2$ (0.203 ηD). The sample was then tested with a CO2-brine. However, de-gassing of the CO2 at the outlet prevented an accurate permeability of the CO2-brine flow, and measured values ranged orders of magnitude higher. The flow test was extended for 75 days. The sample was then flushed with brine-only fluid, and the steady-state, post-exposure permeability$^{187}$ was measured somewhat higher at about $8 \times 10^{-22}$ m$^2$ (0.811 ηD).

Subsequent mineralogical analyses of the mudstones by the authors did not reveal significant alteration resulting from the exposure to CO2 in this testing. However, minor amounts of Ca and SO4 were detected in outflow fluid (probably caused by gypsum dissolution)$^{188}$ The authors also concluded that for the shale samples with an absolute (brine-only) permeability coefficient below $10^{-21}$ m$^2$ (about 1 ηD), no capillary breakthrough of the gas phase was detected up to CO2 pressures of 9 MPa.

The authors concluded that the results show a clear dependence of apparent effective gas permeability on the pressure difference. They also state that the effective CO2 diffusion coefficients determined from pressure transients during leak tests and gas breakthrough tests are on the order of $10^{-10}$ m$^2$/s.

**Al Ismail et al. (2014)** conducted steady state and pulse decay permeability tests on two mudstone samples using He and CO2 gases parallel and perpendicular to bedding. Tests were conducted at a temperature of 38.5 °C, at confining pressures of up to 41.4 MPa and fluid pressures in the range of 2.6 MPa to 13.8 MPa. The two samples are labeled vertical (perpendicular to bedding) and horizontal (parallel to bedding).

The samples were taken from core plugs from the Eagle Ford Shale Formation, which had a high carbonate content (70% in the horizontal sample, 85% in the vertical sample). The

$^{187}$ It took several days of flushing to establish this value.

$^{188}$ A trace amount of cerussite (a form of lead carbonate, PbCO3) was also found on the surface of one of the samples. However, the authors concluded that the likely source of material was from leaching of the confining pressure sleeves.
samples had TOC of about 2% and a total clay content of 10% and 8% for the horizontal and vertical samples respectively.

Tests were conducted on discs, approximately 25 mm in diameter and 5.46 mm (horizontal sample)/5.96 mm (vertical sample) in height. Permeability tests were typically conducted in a series of pulses/steps of alternating He then CO₂ followed He. In a three-step test, the He confining pressure was increased to a maximum of 41.4 MPa and then decreased while at a constant fluid pressure of 13.4 MPa. For the second step, CO₂ was introduced at an increasing confining pressure to a maximum of approximately 29.0 MPa and then decreased while at a constant fluid pressure of 2.6 MPa. The third step was a repeat of the first step with He gas.

Results of the testing indicated the following:

- The measured He and CO₂ gas permeabilities were highly anisotropic, with the horizontal gas permeability 2 to 3 orders greater than the vertical gas permeability in both cases. (The authors concluded that increased permeability was due to the presence of microfracturing and bedding planes in the horizontal direction.)

- The introduction of CO₂ gas into the sample reduced the sample permeability from the initial He permeability for both orientations, with a relatively significant decrease in permeability for the vertical sample, but with only a relatively minor decrease in permeability for the horizontal sample.

- The CO₂ permeability indicated little change with increasing simple effective stress in either sample orientation. (A small increase in permeability was noted upon unloading with the horizontal sample, with little change in the vertical orientation.)

- The initial He gas permeability showed some hysteresis in the loading/unloading cycle, in both the vertical and horizontal direction with a net decrease in permeability upon unloading. Little hysteresis is observed for the final He permeability.

- The effect of CO₂ flow on final He gas permeability also varied with sample orientation. For the vertical sample, CO₂ flow induced a decrease in the subsequent He permeability (in comparison to the initial He permeability), but CO₂ flow induced an increase in subsequent He permeability in the horizontal sample.

- Prior to treatment, the initial vertical He gas permeability of the samples was between 6 and 14 ηD, which decreased with increasing confining stress. The initial horizontal He gas permeability was significantly higher at values ranging from 1.1 to 1.4 µD.
**Guo (2014)** performed permeability and sorption tests with He and CO₂ on a shale sample. Testing was performed at room temperature at a confining pressure of 7 MPa and at gas pressures up to 5.3 MPa. Tests were conducted in a triaxial cell using a transient pulse test method for permeability determinations. The sample was first tested with He and then with CO₂.¹⁸⁹

The sample was from the Green River Shale Formation.¹⁹⁰ The test sample was obtained from a larger rock block recovered at 1,100 m depth and was cored perpendicular to bedding.¹⁹¹ The permeability test sample was prepared as a disc, 2.5 cm in diameter and 1.2 cm in length. The mineral content of these samples was not noted.

Test results for the intact samples with He and CO₂ gas are shown in Figure D2. The data for both gases show a trend of a very small overall increase in permeability with an increase in injection gas pressure up to 5.3 MPa. The CO₂ gas permeability is observed to be significantly less than He gas permeability.

In Figure D2, both permeability curves show a decrease in the trend at 4.3 MPa, which potentially could be related either to the test system/method or due to the rock fabric. The author notes that the test at 4.3 MPa did not come to equilibrium, and attributes the decrease to local swelling in the sample. The author also concluded that sorption is closely linked to apparent permeability.

**Kumar (2014, 2016)** conducted permeability tests on two intact shale samples from Pennsylvania. The source formation(s) of the samples was not mentioned. Samples were tested in a triaxial cell at a confining stress of 10 MPa, using a transient pulse test method to determine gas permeability with both He and CO₂. The temperature for testing was held constant but a specific test temperature was not mentioned (other tests were conducted at room temperature, approximately 20 °C). The gas pressure in the tests ranged from approximately 1 to 6 MPa. Samples were first tested with He and then with CO₂.

The two samples (Samples A and B) were taken from a larger rock block, and were cored parallel to bedding. Test samples were prepared as cylinders, 2.5 cm in diameter and 5 cm in length. The two samples varied in density but had similar water content (1% for Sample A and 0.5% for Sample B). From testing with He gas, the porosity of Sample A was 34%, in contrast to a porosity of 5% for Sample B. The clay content or type of clay minerals in these samples was not noted.

In the testing of Sample A using with He gas, the authors observed permeabilities over a range from about 6 to 10 mD, with increasing permeability with increased gas pressure. He

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¹⁸⁹ It is not clear from the author’s text if separate samples were prepared for each gas pressure measurement, or if the same sample was used in all measurements. The latter is assumed.

¹⁹⁰ No details were provided on the source of the block by the author, except for one reference to Pennsylvania (which may describe the intermediate source of the rock block, i.e., Pennsylvania State University). Source of sample is assumed from Western USA. In addition, no description was provided on the mineralogy of the test sample by the author.

¹⁹¹ Figure in thesis shows the axis of sample core parallel to bedding. However, this may not be tested sample.
permeability was also observed to decrease with increasing confining pressure. However, this decrease with confining pressure was nonlinear.

![Graph showing permeability changes with gas pressure](image)

**Figure D2: He and CO$_2$ gas permeability results with Green River Shale by Guo (2014).**

A significant reduction in permeability was observed in increasing the confining pressure from 10 MPa to 15 MPa, but only a minor decrease in permeability was seen when increasing the confining pressure from 15 MPa to 20 MPa.

Test results for the intact samples with CO$_2$ gas are shown in Figure D3. The data show a small overall decrease in permeability with an increase in CO$_2$ injection gas pressure. No time-dependent response was observed with CO$_2$. At the completion of permeability tests, Sample A was evacuated and a post-test of He permeability was conducted and evaluated. The He gas permeability after testing was observed to be “a fraction of the original He
In addition, the He permeability partly recovered with time during additional He injection.

![Figure D3: CO₂ gas permeability results with intact shales from Pennsylvania by Kumar (2014).](image)

**Notes:**

a. Shale samples (formation unknown) were tested with CO₂ gas; test temperature not known.

In review of the CO₂ data, the authors concluded that the concave form of the permeability curve for Sample A indicates that CO₂ is reacting with the sample. They state that at lower pressures (less than 3.5 MPa), the permeability is dominated by the swelling response of shale, while at higher pressures (greater than 3.5 MPa) the permeability of shale is dominated by the dilation induced by increased pore pressure (i.e., which reduces the effective stress). However, Sample B did not evidence this type of behavior.

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192 The amount is not specified by authors.

193 A similar argument has been applied to CO₂ flow in coal (e.g., Wang et al., 2011).
D.2.2. **FLUID FLOW THROUGH INTACT ROCK AND ARTIFICIAL SAMPLES**

Various fluid flow tests have been conducted with CO₂ on intact mudstones rock samples including Bennion and Bachu (2008), Soldal (2008), Angeli et al. (2009), Berthe et al. (2011), Larsen (2011), Skurtveit et al. (2012), and Liu (2013). In addition, Olabode (2012), and Olabode and Radonjic (2017a, 2017b) have conducted tests on crushed/compacted samples.

The following is a brief synopsis of these experiments:

**Bennion and Bachu (2008)** conducted relative permeability determinations on various rock types using either scCO₂ or H₂S. The samples were taken from core, and from wells drilled southwest of Edmonton, Alberta, Canada. Tests were conducted on two shale samples at a temperature of 43 °C. One sample was from the Colorado Group (the lower portion of the First White Speckled Shale Formation) and the second from the Calmar Shale Formation, from the Winterburn Group.

The Colorado Shale, sampled at 1,618 m, was tested at a confining pressure of 20.0 MPa, while the Calmar, from a depth of 1,566 m was tested at 12.25 MPa. The brines used in testing were to simulate in situ condition, with salinities of 27,100 mg/L and 129,700 mg/L for the Colorado Shale and the Calmar Shale respectively. Test samples were approximately 3.8 cm diameter and 7.5 cm in height.

Prior to testing, samples were cleaned with ethanol or methanol and air dried. After placement in the test cell, samples were saturated with de-aired water then heated and pressurized. The de-aired water was then replaced with CO₂ saturated water (brine). scCO₂ was then injected until core flooding conditions were achieved.

The fluid permeabilities (at 100% saturation) were 78.8 ηD and 2.94 ηD for the Colorado and Calmar samples, respectively. The relative permeability curves provided for the shales show a reduced range for relative permeability in comparison to the sandstone and carbonate units. The relative permeability curves of the shales were limited to be within a range of CO₂ saturation of 0 to 40% and indicated essentially no brine relative permeability above a CO₂ saturation of 40%. The maximum relative permeability values for CO₂ were also small, and for the Colorado sample, the maximum value was only about 0.015.

Time-dependent effects were not discussed. Overall, the authors noted that H₂S brine is much more aggressive than the CO₂ brine, with the relative permeability value for H₂S greater than the CO₂ value at the same saturation. The Colorado Shale had a brine permeability of 78.8 ηD, and the permeability of the Calmar Shale was measured at 2.94 ηD.

**Soldal (2008) and Angeli et al. (2009)** conducted break-through tests on a claystone together with deformation monitoring. The sample was from the core which was drilled 1,360 meters beneath sea level (at a water depth of about 350 m), in a well in the North Sea, approximately 65 km off the Norwegian coast, west of Bergen, Norway. The claystone is from the Upper Jurassic Draupne Formation which typically has an average TOC of between 5 and 10 wt%. From XRD analysis, the sample has a clay content of about 39.5% (14.6% smectite, 9.2% illite, 12.3% kaolinite, and 3.4% chlorite) with about a 14.6% carbonate content and 6.1% pyrite.

Tests were conducted in a triaxial cell, and both axial and lateral deformation was measured during testing together with seismic velocities (P- and S-wave). The sample was subjected to
a confining pressure of 13 MPa, a base pore pressure of 8 MPa and a temperature of 36 °C. The sample was first saturated in a brine for 10 days, then partially pressurized, followed by heating to the test temperature and finally pressurized to the final pressure. The brine for the test was prepared as a mixture of distilled water and NaCl (57 g/L).

The test sample used in the test program was cylindrical in shape and with initial dimensions of approximately 38 mm in diameter and 40 mm in height. In addition, the sample was an older specimen, having been stored approximately nine years (1998 to 2007) prior to testing. Efforts had been made to limit drying by double-wrapping the core in plastic, applying an axial load, and storing the sample in wet room. The sample, however, did evidence effects of drying including salt crystal formation on the exterior and visible fracturing.

Testing included an initial permeability test with brine followed by a flow test with scCO₂. The flow testing was conceptually performed in two stages, starting with a first stage of conducting a breakthrough test, followed by a second stage of maintaining the flow for 30 days to observe changes in the behavior of the sample.

A permeability test with the brine was conducted over a period of ten days at a differential pressure of 0.8 MPa as reported by Soldal (2008). The permeability coefficient was computed periodically during this test. The resulting coefficient was variable and somewhat cyclical, ranging from 5.78 to $8.15 \times 10^{-13}$ m/s. The variation in the coefficient corresponded directly to variation in the cell temperature. During this period, the axial dimension experienced a minor decrease, while the lateral deformation showed little change.

The pore pressure gradient of the flow test was continuously increased from the start of the test up to approximately 11.9 MPa at day 31 (at the completion of the breakout) and then maintained at this pressure to day 63. The results indicated no flow at pressures below 3.5 MPa. At higher pressures, the flow at the inlet portal started to increase, as CO₂ started to enter the sample at about day 4. Fluid flow at the outlet portal started at about day 26, showed an increase at day 31, and continued to slowly increase thereafter with the flow rate becoming linear at day 58.

The lateral/radial deformation of the sample was essentially constant up to day 26 and then expanded rapidly, reaching an asymptotic maximum value at about day 36 (and remained at this value thereafter). The axial strain displayed minor variations up to day 31 and then decreased at a constant rate to day 63. The P-wave velocity showed a similar trend, being roughly constant prior to day 31, and then continually decreasing in stages to day 63.

Upon inspection of the final sample, Angeli et al. noted that larger voids (i.e., greater than approximately 100 μm in dimension) showed no effect of dissolution, but the distribution of smaller voids (smaller than 10 μm) at the inlet side of the sample (bottom) apparently decreased significantly. In addition, the authors noted that the test sample contained an increased amount of H₂O and that (during testing) the outlet fluid contained a large amount of gas, with a significant quantity (1%) of hydrogen gas (H₂).

The authors concluded that these test results strongly indicate that the flow of CO₂ was along a few high permeable pathways due to re-opening of existing fractures.
Berthe et al. (2011) conducted two concurrent through-diffusion laboratory experiments with Tournemire claystone. One test was conducted with a brine developed to simulate the local groundwater together with N₂ pressure; the second test included a CO₂-saturated version of the brine under CO₂ pressure.

The test samples were mudstones from the argillaceous formation of Toarcian age at the experimental site of the French Institute for Radiological Protection, near Tournemire, France, taken at a depth of 15 m under the tunnel invert. The clay content of the formation ranges from 40% to 50% and consists of mica, kaolinite, illite, and illite/smectite mixed-layers (with more than 70% of illite and chlorite). Calcite content varies from 10% to 20%.

In explanation, a through-diffusion method sandwiches a test sample between two more-permeable “reservoirs”. The upstream or source reservoir contains a constant concentration of tracers and a downstream or collection reservoir which is monitored for the incoming flux of tracers. A CO₂ pressure of 0.1 MPa was applied in the upstream reservoir. The setup establishes a concentration gradient and the first Fick's law can be used for determining tracers’ diffusive parameters. Tests were conducted for approximately 400 days. The samples were tested perpendicular to top bedding. During this testing, the following was monitored: pH, Na, K, Mg, Ca, Cl, SO₄, TOC, and alkalinity.

During the initial part of the testing, monitoring of the flux non-radioactive tracers for 60 days indicated diffusion values for the brine-only test of about 81 x 10⁻³¹ m/s for deuterium and 8.1 x 10⁻³¹ m/s for bromide. In contrast, the CO₂-brine test indicated diffusion values of 116 x 10⁻³¹ m/s and 18.5 x 10⁻³¹ m/s for deuterium and bromide respectively, a substantial increase for both tracers from the base case. Porosity estimates for the samples showed a similar trend of increase with the CO₂ exposure.

One year after this test sequence, a second test sequence performed with radioactive tracers, indicating diffusion values of about 76 x 10⁻³¹ m/s and 6.4 x 10⁻³¹ m/s for tritium and Cl-36 respectively for the brine-only sample, and values of 111 x 10⁻³¹ m/s and 20.8 x 10⁻³¹ m/s for tritium and Cl-36 respectively for the CO₂-brine sample, confirming the differences observed earlier. The authors noted that the flux values for the brine-only samples were comparable to values obtained by others. Porosity estimates for the samples showed a similar trend of increase with the CO₂ exposure, with the porosity values for Br increasing from 2% to 6% and for Cl-36 from 3% to 6%.

As noted by the authors, over the monitoring period of about 390 days, the concentrations of Cl, SO₄, Na, K, and TOC as well as pH remained relatively constant and were highly similar for both brine-only and CO₂-brine samples. However, there was a substantial increase of the Ca, Mg concentrations and alkalinity with time in the CO₂-brine test, as shown in Figure D4. Note that these curves show a significant rate change at roughly day 70.

194 The tunnel is about 250 m below surface as part of a test facility.
195 The authors do not mention a test temperature; a temperature of about 20 °C is probable.
196 However, Na and Cl did show some variability over the period, especially at times less than 200 days.
Notes:

a Partial results of a through-diffusion test with CO2-brine and brine-only on claystone samples from near Tournemire, France. Concentrations of Cl, SO4, Na, K, and TOC, as well as pH, remained relatively constant over the same period.

Figure D4: Changes in geochemistry from diffusion tests by Berthe et al. (2011).

**Larsen (2011)** conducted permeability tests and CO2-breakthrough tests on different types of shales. The samples were from two units: (1) the Lea Park Shale Formation and (2) the Colorado Shale Formation. The Lea Park Shale samples were a dark gray shale of Upper Cretaceous age from a boring near Weyburn, Saskatchewan at a depth of approximately 602 m to 611 m. The Colorado Shale samples were from a boring near Rocanville, Saskatchewan from a depth of about 427 to 430 m.

From optical microscopy testing, the tested Lea Park unit had a carbonate content of about 8%, a clay content of about 23.7%, and a 5% organic content. From XRD analysis, the clay content was composed of 10% kaolinite, 9.2% illite, and 1.4% chlorite with smectite present.

The Colorado Shale samples were described as “mid very-fine-grained argillaceous calcilithite”, a unit with a high carbonate content (about 48.3%), a low clay content (about 4.2%), and an organic content of 35.8% based on optical microscopy. From XRD analysis, the clay content was composed of 1.1% kaolinite and 1.3% illite with smectite present. Samples from both units were considered very friable in sample preparation and handling. The water content of the samples was not reported.
An artificial brine was used for testing. Tests were conducted in a triaxial cell at a confining pressure of 14.5 MPa, a back pressure of 7.5 MPa and at room temperature (25 °C). Samples were consolidated in 0.5 MPa increments with each increment stabilized over a period of 24 hours. Transient pulse permeability measurements were made on the samples with a pressure pulse of approximately 0.7 MPa.

Samples were cylinders with a low aspect ratio (with heights of 5.5 to 6.4 cm and diameters of 7.6 to 7.7 cm). Permeability tests were conducted with brine on four samples (two of each rock type) and three breakthrough tests were also conducted with liquid CO2.

Results of the program were:

- Permeability results for samples from the Lea Park Shale ranged from 14 to 35 ηD (five tests) and between 8 and 46 ηD (two tests) for the Colorado Shale.
- The CO2 breakthrough pressure for the Lea Park Shale was measured at 0.02 MPa, while values of 0.02 and 2.7 MPa were measured for the Colorado Shale. The 0.02 MPa value is low and suggests a low capillary sealing capacity for the units.
- The obtained test results were found to be comparable to test results in the literature (e.g., Pierre Shale, and shales from Scotian Shelf and the North Sea).

No observations were made on alteration, swell or time-dependent aspects of CO2 flow.

Skurtveit et al. (2012) conducted scCO2 breakout experiments with two samples from the North Sea area. The two test samples (labeled Draupne I and II) came from the Upper Jurassic Draupne Formation, from a well located in the Troll East area in the northern part of the North Sea. The formation is essentially homogeneous and anisotropic. The test core was sampled at about 1,057 m depth, and no swelling was observed in handling the material. The Draupne samples were low-carbonate shales, composed of 40% to 70% clay minerals (mainly smectite, kaolinite, and illite) with traces of pyrite and dolomite; the TOC is about 2%.

The breakthrough testing was conducted using a triaxial cell, allowing the measurement of axial and radial strains during testing as well as fluid pressures. Axial ultrasonic compressional (P) and shear (S) wave velocities were also measured. The cylindrical plugs used in the cell were about 38 mm in diameter and about 40 mm in height.

The test system (cell and pumps) was placed inside a separate cabinet to maintain a uniform temperature; test temperature in the cabinet varied with test phase and sample. All brine testing was conducted at 20 °C. For the CO2 testing phase, the Draupne I test was conducted at a temperature of 36 °C and the Draupne II testing was conducted at a temperature of 40 °C. Samples were scanned before and after testing.

197 The “Lea Park brine” used for testing was composed of (mg/L): CaCl2: 122.2; NaCl: 2,870.7; Na2SO4: 3,849.1; NaHCO3: 216.7; KCl: 16.8 and MgSO4: 31.0.
Of importance, the samples were cored and stored 9 years prior to testing. Attempts were made to limit moisture loss. Upon initial sampling, the rock cores were wrapped in plastic and aluminum foil and then dipped in hot wax.\textsuperscript{198} After sample plugs were drilled from these cores, the plugs were placed in several plastic bags with moist paper and then placed in a storage room. However, when retrieved prior to testing, the samples showed evidence of drying (such as salt precipitation). In addition, the drying of the samples induced microfractures as X-ray CT scans revealed patterns of cracks in the samples.

Briefly, the test procedure consisted of two stages; the first stage involving brine-saturation of the sample to define baseline conditions followed by a second stage with CO\textsubscript{2} breakthrough testing with flows at various pressure and stress conditions. Due to the low permeability of the samples, the duration of the first stage was 5 weeks for Draupne I and 20 weeks for the Draupne II. The second stage of the tests lasted 15 to 19 weeks.

The results of the brine-testing stage indicated that the permeabilities\textsuperscript{199} of the samples were a function of confining stress, suggesting that flow was affected by the observed microfracturing. In addition, a loading/unloading cycle performed with the Draupne II sample showed large hysteresis in axial strain, with a cutoff at 4 MPa, again suggesting fractures opening at lower pressures. In more detail, the brine permeability of Draupne I was 61.1 $\eta \text{D}$ at 13 MPa confining pressure; the permeability of Draupne II was 5.6 to 6.5 $\eta \text{D}$ at a confining pressure of 21.7 MPa, and 12.3 $\eta \text{D}$ at 16.8 MPa.

The following was observed by the authors for the Stage 2 CO\textsubscript{2} breakout tests:

- Two breakout tests were performed with Draupne II, as the first test at a confining stress of 19.7 MPa was unsuccessful (a breakout was not achieved with the equipment). The second test at a confining stress of 14.8 MPa was successful. Draupne I was successful at a confining pressure of 13.5 MPa.
- For both successful breakthrough experiments, the samples started to dilate in the radial direction just before breakthrough, with greater total dilation in Draupne I compared to Draupne II. In addition, Draupne II showed dilation in the axial direction prior to breakout.
- There was a large hysteresis between the effective CO\textsubscript{2} permeability measured directly after breakthrough and the measured values after CO\textsubscript{2} flow was re-established. Different permeabilities were obtained at the same pore pressure difference due to different confining pressures.
- The data suggested a functional dependency between the effective permeability and sample deformation. Both absolute and effective permeability increased when the

\textsuperscript{198} A process sometimes called, “seal-peel.”

\textsuperscript{199} Permeabilities determined by brine flow are considered absolute permeabilities. Effective permeability for CO\textsubscript{2} was calculated after breakthrough when steady state flow out of the sample was observed, assuming a 100\% CO\textsubscript{2} flow out of the sample.
sample dilated. The effective CO2 permeability was more sensitive to changes in volumetric deformation and it seems to be similar to a power-law relationship.

- Due to high variability with ultrasonic velocities with Draupne I, only P-wave and S-wave from Draupne II were analyzed. With Draupne II, the resultant P-wave and S-wave velocity data were initially considered “high quality” before the introduction of CO2 but they were “significantly deteriorated” after CO2 breakthrough. The velocity values were directly proportional to applied loading (and increased with loading and decreased with unloading). The relatively higher ultrasonic velocities during the unloading process compared to the loading process indicated that some porosity did not reopen with unloading and the sample suffered permanent deformation. This indicated that load (compaction) history influences permeability.

- The ultrasonic velocities from Draupne II decreased dramatically after breakthrough. The authors suggested that the change was caused by both fluid and mechanical effects. Fluid effects alone (i.e., the density change from the replacement of brine by CO2) were considered insufficient to cause the observed decrease. The decreased velocities together with the dilation data suggest that the mechanical effects are caused by the pressure-induced opening of microfractures.

- Measurements of effective CO2 permeabilities under varying pressure conditions after CO2 breakthrough showed a reduction in CO2 permeability as the pore pressure difference across the sample decreased until flow stopped at a sufficiently low pore pressure difference. Re-establishment of the flow started at a lower injection pressure than the initial breakthrough and lower permeability values were observed during the re-established flow.

- Comparison of the pre- and post-test fracture X-ray scans indicate that the post-test fractures are fewer and more closed than the fractures observed in the pre-test scan.

Liu (2013) conducted two scCO2 breakthrough tests and two permeability tests with a friable Canadian shale. Two test samples used in the program (labeled LP1 and LP2) were a fissured clayey shale from the Late Cretaceous Lea Park Formation, taken at a depth of approximately 1,530 to 1,533 m in the Pembina Cardium oil field in west-central Alberta, Canada. Testing indicated that this shale has a total clay content of approximately 38% (composed of 22.0% illite, 10.0% chlorite and 6.0% kaolinite) together with a negligible carbonate content. Due to the friable nature of the shale, samples were hand-shaped, and it was observed that the material contained a substantial number of small fissures.

Samples for permeability testing were trimmed to short cylinders. LP1 had a diameter of 60.10 mm and a height of 26.70 mm; LP2 had a diameter of 65.21 mm and a height of

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200 The author also conducted chemical batch reaction tests with the same rock unit, reported elsewhere in this report.

201 This testing is also briefly described in an abstract (see Liu and Chalaturnyk, 2012).

202 The uniaxial strength of the unit is about 310 kPa, as reported by others (e.g., Henry, 2014, Appendix B), which suggests the unit is more of an overconsolidated clay then a rock.
26.70 mm. A synthetic brine 3 g/L NaCl was used as a pore fluid. Permeability measurements were conducted using the pulse decay method prior to performing capillary entry pressure measurements at a temperature of 50 °C. Tests were performed at a back pressure of 15 MPa.

The measured permeability with sample LP1 was 0.22 \( \eta D \) at a confining pressure of 28.5 MPa; LP2 was evaluated at confining pressures of 28.5 MPa, 30.0 MPa, 31.5 MPa and 33.0 MPa with resulting permeabilities of 0.44 \( \eta D \), 1.45 \( \eta D \), 0.43 \( \eta D \), 0.16 \( \eta D \), respectively. As noted by the author, the results did not suggest a correlation of permeability with confining stress.

Capillary pressure measurements with scCO2 were conducted with LP1 and LP2. However, the large pressure steps with LP1 only allowed a rough assessment of entry pressure of between 500 and 1,000 kPa. Testing with LP2 indicated an entry pressure of 700 kPa.

In summary, testing indicated that Lea Park Shale had a low capillary entry pressure (700 kPa) for CO2 and a low fluid permeability (varying from 0.16 \( \eta D \) to 1.45 \( \eta D \)) at 50 °C at a confining pressure of 28.5 to 33.0 MPa.

**Olabode (2012)**\(^{203}\) conducted core flood experiments with crushed shale samples and a synthetic brine to investigate geochemical changes in shale caprocks. Crushed samples of shale core from the Pottsville Formation of the late Paleozoic Black Warrior Basin, AL, were flooded with CO2-brine for a period of 92 days at elevated pressure. The samples were subjected to a flow rate of 0.3 cm\(^3\)/min at a back pressure of 6.69 MPa and at 25 °C temperature.

The test cells were constructed of stainless steel and polyether ether ketone materials for corrosion resistance. A brine solution was passed through the crushed shale specimen in a one-pass configuration and characterized before and after flow through the cell. Samples were assembled from core from several wells, and the samples were crushed\(^{204}\) and packed into cells. Conditions for core storage or drying of samples were not described. XRD and energy dispersive spectroscopy and geochemical analyses were used for characterization.

The CO2-brine used in this testing was based on a solution of distilled water with primarily NaCl and a small amount of KCl.\(^{205}\) (The synthetic brine was designed to simulate West Texas Formation fluids.) In addition, CO2 was bubbled through the solution at 0.17 MPa (25 psi) for approximately 80 minutes, resulting in average pH 3.9 as for the inlet/source solution for testing.

Three samples were created from the core samples and labeled A, B and C. The clay mineral fraction was significant in all the samples with total clay contents of approximately 75.1%, 65.0% and 47.5% in samples A, B, and C, respectively. The clay minerals included common mica, chlorite, and kaolinite, but the amount of each of these minerals was not described. The
remaining mineral content of the samples was quartz with a minor amount of feldspar; the carbonate content of the samples was negligible.

The experimental program consisted of core flooding the three samples in parallel. The test duration for the program was 92 days, with the samples subjected to fresh CO₂-brine over the entire period.

From the testing of the combined outflow of all three samples, the pH profile of the samples rapidly declined from about 8 to 5.5 in the first 20 days of testing, but eventually reached an equilibrium regime at a pH 6.5 and thereafter, extending to day 70. However, at day 70, the pH again decreased sharply to a final value of 5 at 92 days. The variation demonstrates the ability of the samples to buffer the brine flow for some time without calcite.

XRD analysis of the samples before and after testing showed only subtle changes in the three samples over 92 days and the extent of these changes varied with each sample. Sample A showed an increase in the ratio of feldspar to muscovite and chlorite, with an increasing muscovite and chlorite with test duration. Sample B showed a decrease in muscovite and an increase in chlorite, but the feldspar seemed unchanged. For Sample C, the albite ratio to feldspar increased, and kaolinite ratio to feldspar decreased, but other components remained the same, in contrast to the other 2 samples.

Test results also indicated that the bulk specific surface areas for the three samples show a general tendency for the surface area to increase with CO₂-brine flooding duration, but the rate slows with increased time. Sample C, however, showed a decrease in the first month, increasing only after this point with time. Evaluation of the pore size as a function of the bulk specific surface area indicated that the most impact of the core flood on pore diameter was variable with time but overall, the most change occurred in pore diameters less than 3.5 ηm in diameter.

The authors concluded that the response of the samples was controlled by minute geochemical changes that are hard to detect particularly at the submicron level. They also recommended that future experimental work needs to investigate the importance of temperature on geochemical changes that affect the specific surface area and pore network of shale as well as to study the impact of geochemical reactivity on fractures.

Olabode and Radonjic (2017a, b) performed flow tests with CO₂-enriched brine on artificial samples (composed of fractured mudstones) together with micro-indentation testing.

Tests samples were from four formations with some to moderate clay content: 1) Sample A: Mancos Shale; 2) Sample B: Marcellus Shale, 3) Sample C: Pottsville Formation; and 4) Sample D: Wilcox Formation. The mineralogy of Sample A was composed of approximately 20% clay minerals, 15% carbonates (i.e., calcite, dolomite, and anhydrite) and 65% other minerals (quartz, feldspar, plagioclase, and pyrite). Sample B was composed of about 22% clay, 28% carbonates and 50% other minerals. Samples C and D had similar mineralogy with about 44% clay, 1% calcite and 55% other. The clay minerals were predominately chlorite, illite, and kaolinite.
A sample of crushed rock (i.e., a packed bed)\textsuperscript{206}, was formed for each rock type, and permeabilities determined using the GRI method\textsuperscript{207}. The brine used in the testing was a saline solution prepared using distilled/de-ionized water with sodium chloride (0.35 mol/L NaCl) and a trace amount of KCl (less than 0.005\%). The brine was saturated with CO$_2$ by bubbling CO$_2$ gas into the brine at 0.41 MPa for 2 hours.

The flow experiments were conducted at 50 °C and conducted three times for each rock unit. Each sample was subjected to a flow rate of 0.5 cm$^3$/min at a regulated back pressure of 6.9 MPa. Duration of each experiment was 5 days (approximately 120 hours).

Micro-indentation testing of the samples was performed with a maximum force 10 N (with a contact load of 30 mN). Loading and unloading rates were 10 N/min with a pause at the maximum load of 30 seconds.

Results from fluid monitoring indicated that elemental concentration trends varied from sample to sample. In detail:

- For Sample A, the concentration of elements S, selenium (Se), Ca, Mg, K, and B showed an immediate increase in concentration, but then (in a reversal) the value decreased with time. The concentration of Zinc (Zn) evidenced an initial increase but stabilized thereafter. The concentrations of As, Si, and P were variable over the test. The concentrations of elements Mn, Al, Fe and nickel (Ni) showed little change with time.

- For Sample B, concentrations of K, Al, Zn, P, Ni, As and B showed an initial decrease but then stabilized thereafter. Concentrations of Ca, Mn, sulfur (S), and Si increased initially but then decreased with time. Concentrations of Mn, Se, and Fe showed little change with time.

- For Sample C, concentrations of K, Si, Se, and B showed an initial increase but then decreased with time. Ca and Mg concentration initially increased and then stabilized thereafter. The concentration of Zn decreased initially but then stabilized thereafter. The concentrations of P and As were variable over the test duration. Concentrations of Mn, S, Al, Fe, and Ni showed little change with time.

- For Sample D, an immediate increase of the concentration of elements Mn, S, Ca, Mg, Fe and P was noted, but these increases tended towards zero at the end of 5 days. Zn, K, Al, Ni, As and B evidenced an initial decrease, which then generally reached an equilibrium level. Si evidenced an initial increase which then generally reached an equilibrium level. Se concentrations showed no change over the test duration.

Comparison of Vicker's microhardness from micro-indentation tests indicated that there was a small decrease in the post-test values in comparison to pre-test values in three samples (in Samples A, B, and D) and a small increase in the values for Sample C. Hardness changed in

\textsuperscript{206} Crushed to 1 to 2 mm in diameter.

\textsuperscript{207} The GRI method, also known as the crushed rock method is from the Gas Research Institute; see Guidry et al. (1995) and Sander et al. (2017).
the order of A, D, B (with A showing the most decrease). Comparison of these hardness changes with mineralogy test result suggests a general correlation of increasing hardness (i.e., decreasing change) with increasing quartz content, with Sample C showing a small increase in hardness with the highest quartz content (of about 11%).

Estimates of sample permeability (with a fracture conductivity model) indicated that the dimensionless fracture conductivity (expressed in a series of equations and labeled here as $C_r$) for flow for all four samples decreased rapidly during the first day of testing, but then decreased more slowly with time (at about a constant rate) for the remainder of the test, reaching a value of approximately $3.8 \times 10^{-6}$ $C_r$ at 5 days. The decrease in response was most prominent for Sample A, decreasing from an initial value of about $6.6 \times 10^{-6}$ to $3.9 \times 10^{-6}$ $C_r$, and the least evident was Sample B, with a decrease from an initial value of about $4.0 \times 10^{-6}$ to roughly $3.75 \times 10^{-6}$ $C_r$.

XRD analyses by Olabode and Radonjic (2017b) on these samples indicated little to no change in mineralogical content in the samples after CO$_2$-brine exposure, but the increased peaks in the XRD results suggested that the most amorphous content of the samples had been removed by the acidic fluid. In addition, bulk rock compositional analyses indicated that there were slight changes in quartz, carbonates and clay contents of the samples. In more detail, Sample B showed a significant gain in illite (10.12%), while Sample C showed a significant loss in illite (-9.83%). In addition, Sample C evidenced a significant increase in quartz (11.19%) as well. Ca was the predominate element leached from the samples, which led to the formation of new diagenetic minerals. There was also an increased amount of total carbon content of all four samples.

**D.2.3. EFFECTS OF CO$_2$ ON FRACTURE FLOW**

Limited fluid flow-through and breakout tests on fractured samples have been conducted with mudstones samples. In more detail, these types of experiments are described in: Andreani et al. (2008), Alnoaimi and Kovscek (2013), Crandall and Bromhal (2013, 2014), Edlmann et al. (2013), Smith et al. (2013), Kumar (2014), Kumar et al. (2016), Carey et al. (2015), Li (2016), Li et al. (2016), van Noort and Yarushina (2016a), and Zhou et al. (2016).

The following are summaries and significant findings from these researchers in chronological order:

**Andreani et al. (2008)** conducted two flow-through tests with claystones having artificial fractures and using both CO$_2$-brine and CO$_2$-gas. The claystone was from the Upper Toarcian formation sampled near Tournemire, France. The samples had a clay mineral content of about 45 vol% (24% kaolinite, 10% muscovite, 10% interstratified illite/smectite and 1% chlorite) and 27 vol% carbonate (25% calcite, 2% siderite), with a trace of pyrite (3%).

For each test, a cylindrical sample with a diameter of 9 mm and a length of 15 mm was drilled from a claystone core. A planar fracture was created in this sample by sawing the cylinder longitudinally in half, and then tying the two parts together with a fiberglass-loaded epoxy resin, resulting in a fracture width of 7 mm. The sample sides were covered with a glued plastic sheet, leaving the two ends exposed.
The samples were first saturated with a “claystone-equilibrated water”, which was prepared by mixing powdered claystone with distilled water for two months until equilibrium was achieved (after about 5 weeks). The samples were then placed in a flow-through reactor for testing. The confining pressure on the sample was maintained equal to the inlet fluid pressure, and the outlet pressure was maintained at a pressure slightly higher than 0.12 MPa. The two tests were performed at 25 °C. The CO2-brine was injected at a constant flow rate of 6.94 x 10^{-9} m^3/s (0.6 L/day).

The samples were exposed to cycles of alternating flows of CO2-brine and CO2-gas (starting with CO2-brine and ending with CO2-brine), Test #1 involved 4 cycles and Test #2 performed 2 cycles. The CO2-brine was formulated to be representative of a “carbonate-reservoir” brine and was made using distilled water and laboratory-grade salts. This brine was subsequently saturated with CO2 at a partial pressure of 0.12 MPa. The CO2-gas was water-saturated CO2 gas. The cycles were of varying duration. The total test time for Test #1 was approximately 792 hours (33 days), with cyclic testing begun at a test time of 280 hours (after sample saturation), resulting in a cycling period of about 512 hours.

In reviewing results, the authors focus on the longer Test #1. For Test #1, the hydraulic aperture increased in a stair-step fashion. The aperture increased after each gas-CO2 period, as measured at the start of the CO2-brine period, and then remained relatively constant over the remaining period. The authors observed that for both experiments, the increase of hydraulic aperture at the beginning of each CO2-brine flow period scales linearly with the duration of the preceding CO2-brine flow period, but it is independent of the duration of the preceding CO2-gas flow period. The authors concluded that the permeability increase (and associated aperture increase) was due to the widening of the fracture from expelling a thin layer of clay particles as soon as CO2-brine flow replaces CO2-gas flow. Specifically, the volume of clay particles detached from fracture walls at the beginning of a given CO2-brine flow period is controlled by the thickness of the altered layer affected by clay decohesion during the previous CO2-gas flow period. The thickness corresponds to the high porosity zone where both calcite and quartz were dissolved during the preceding CO2-brine flow period. The authors also described the process in the following terms: During CO2-brine flow, permeability of the altered zone is not significantly changed because clay particles form a continuous framework. However, the following CO2-gas flow decreases the cohesion of clay particles and the particles are then transported by the next CO2-brine flow, thereby changing aperture and permeability.

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208 Composition of “claystone-equilibrated water” (mol/kg): 6.05 x 10^{-4} Ca; 6.80 x 10^{-5} Mg; 6.87 x 10^{-5} K; 1.38 x 10^{-4} Na; 1.29 x 10^{-6} Fe; 2.93 x 10^{-6} Al; 7.38 x 10^{-5} Si; pH 7.7; 9.3 x 10^{-5} ionic strength.

209 The authors also describe the process in the following terms: During CO2-brine flow, permeability of the altered zone is not significantly changed because clay particles form a continuous framework. However, the following CO2-gas flow decreases the cohesion of clay particles and the particles are then transported by the next CO2-brine flow, thereby changing aperture and permeability.
The authors also observed the following on the geochemistry:

- After the first CO2-brine injection, the K concentration increased progressively up to the reservoir K composition and then remained relatively stable until the end of the experiment.

- Ca concentration of the outlet fluid increased above the Ca inlet fluid composition and finally trended asymptotically to the inlet fluid composition, indicating that Ca was continuously released from the sample.

- Outlet Si concentration measured during the three first cycles indicated that Si was also being steadily released during the CO2-brine flow periods. The authors state that the release was related to dissolved clay and/or clay particles in the sample, and the dissolution of quartz grains.

Alnoaimi and Kovscek (2013) conducted low-pressure and high-pressure sorption measurements together with permeability measurements on samples of Eagle Ford Shale with various gases. The test samples were from a calcareous mudstone unit of the Eagle Ford Shale play taken from horizontal core, which was sampled at a depth of 3,887.2 m (12,753.3 ft). The unit had a carbonate content of 53.3 wgt% and a clay mineral content of 12.3 wgt%. The unit also had a trace of pyrite (4.7 wgt%) and a TOC of 4.8 wgt%.

Permeability testing was conducted with He, CH4 and CO2 gases, using a pressure pulse decay approach. The permeability test was performed on a sample plug, 2.5 cm in diameter and 4.6 cm in length. Of significance, the sample had a clear-calcite-filled fracture, which ran roughly longitudinally through the entire sample (i.e., parallel to the core axis). Prior to permeability testing, the sample was heated in a vacuum oven for 3 days at 65.5 °C to remove residual moisture. The sample was then double wrapped using layers of heat-shrink Teflon tubing, and aluminum foil and nickel foil. Permeability tests were performed at an effective stress of 3.45 MPa (500 psi) with a differential stress across the specimen of 0.17 MPa (25 psi).

Sorption testing was performed with a small fragment from an end trim of the core plug, which was pulverized210 prior to testing. Low-pressure sorption was conducted with N2 at -196.15 °C using the non-localized density functional theory (NLDFT). (The NLDFT method describes effectively the sorption process at mesoporous and microporous levels by matching the experimental isotherms to modeled isotherms.) In addition, high-pressure sorption measurements were conducted on the core plug, using the transient pressure pulse decay apparatus.

The low-pressure sorption test results from the program indicated that the total amount of gas adsorbed by Eagle Ford sample at standard pressure and temperature (STP211) was about 31 cm³/g. This was compared to a value for Barnett Shale (obtained elsewhere) of 25 cm³/g.

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210 The sample was manually crushed and sieved to a size between 45 µm and 63 µm.

211 Assumed to be a temperature of 273.15 K (0 °C, 32 °F) and an absolute pressure of exactly 100 kPa (0.1 MPa, 1 bar).
Comparison of the sorption curves from these two mudstones indicated that while the two curves were similar in trend, the Eagle Ford values were higher (for the entire range of relative pressure) and that the hysteresis in the Eagle Ford curve appeared to be larger than the Barnett sample, potentially indicating greater capillary condensation, as noted by the authors.

The total pore volumes of the Eagle Ford and Barnett samples as obtained by NLDFT were 0.04 cm³/g and 0.03 cm³/g, respectively with an average pore diameter of 13.9 nm and 28.1 nm, respectively. These average pore diameters correspond to 50% of the pore volume that exist below an 80 nm pore diameter.

The high-pressure sorption isotherm for CO₂ reached a maximum of about 250 scf/ton at a pressure of about 4.5 MPa (650 psi). The isotherm initially shows a decreasing rate until about midway in the pressure range, then sharply increases to the final value; the inflection in rate occurs at about 2.4 MPa (350 psi). The absolute sorption isotherm for CH₄ reached a maximum of about 40 scf/ton at a pressure of about 5.5 MPa (800 psi). This isotherm shows a typical Langmuir shape with no inflection point.

From permeability data, adjusted permeability values (matching simultaneously the upstream and downstream pressure histories) indicated that the permeabilities of all three gases were approximately inversely (linearly) proportional to pore pressure (Klinkenberg effect; see Klinkenberg, 1941). The intrinsic permeability (i.e., the y-axis intercept of the linear fit at infinite pressure) for CO₂, CH₄, and He were essentially identical with values of 12.25 µD, 31.1 µD and 12.5 µD respectively. The trend of the slope with pore pressure of CH₄ and He were close but the slope of CO₂ was substantially lower and thereby showing less of an effect of pore pressure.

In summary, the similarity in permeability results between He and CO₂ indicate the absence of short-term effects on the mudstone permeability during this testing with CO₂ (i.e., such as swell and sorption). In addition, the high intrinsic permeability values obtained with all three gases indicates that flow through the core was probably dominated by the presence of the central fracture.

Crandall and Bromhal (2013, 2014) conducted a series of four CO₂-saturated-brine flow experiments on fractured mudstones from three different sites.

The three rock types tested were:

1. **Kirtland Shale**: The sample was from the Upper Kirtland Shale Formation, cored in a well in the north-central portion of the San Juan Basin, New Mexico and sampled at a depth of 624.5 m (2,049 ft). The sample was specially sealed in the field after coring. The friable nature of the unit required a unique sub-coring process together with use a thin layer of epoxy. The flow was along natural fractures.

2. **Eau Claire mudstone**: This sample was from the bottom of the Lombard Member of the Eau Claire Shale Formation, cored in a well in Morgan County Illinois, and sampled at a depth of 1,174.7 m (3,854 ft). A rough longitudinal fracture was induced in the samples for testing using a modified Brazilian test technique. Two samples were prepared from this unit.
3. **Tuscaloosa claystone**: The sample was from the Lower Tuscaloosa Formation, and cored in Jackson County, near Escatawpa Mississippi. It was sampled at a depth of 2,612 m (8,569.75 ft). The sample axis was oriented parallel to bedding and appeared slightly desiccated prior to testing with some bedding planes separation. Given the orientation, no induced fracture was required for testing.

The specific mineralogy of these samples was not discussed in the paper.

Special artificial brines were employed for each sample for testing. Testing with Kirtland Shale used a primarily NaCl-based brine, while testing with Eau Claire mudstone and Tuscaloosa claystone incorporated significant amounts of CaCl₂ and other salts.

Test conditions also varied with each rock type, depending on the original in situ conditions. The Kirtland sample was tested for 25 days using a constant injection pressure of 11.17 MPa (1,620 psi), a controlled temperature of 27 °C (80.6 °F) and a confining pressure of 12.76 MPa (1,850 psi). The two Eau Claire samples were tested at room temperature, and a confining stress of 12.76 MPa (1,850 psi). One Eau Claire sample was tested at an injection rate of 0.013 mL/min for 22 days, while the second one was tested at 0.026 mL/min over 19 days, with fluid pressures varying between 11.03 and 11.72 MPa (1,600 and 1,700 psi). The Tuscaloosa sample was tested at room temperature for 39 days at a confining stress of 27.58 MPa (4,000 psi) and at an injection rate of 0.013 mL/min.

The samples were injected with the appropriate brine saturated with CO₂ over the duration of the test. Axial and lateral pressures were applied during flow testing using a Hassler-style triaxial pressure vessel. The core was surveyed using dual-energy CT scanning and X-ray fluorescence methods together with elemental brine analysis.

Results of the testing with the Kirtland samples indicated:

- The core was heterogeneous, with both high-density zones and fracture zones throughout the core.
- The fractures in the sample were small compared to image resolution.
- The fracturing along the core was non-uniform. There was no discernible primary fluid pathway through the core, but several lateral fractures were noted.

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212 The Upper Kirtland clay mineral fractions are dominated by smectite and illite or mica together with a significant iron-bearing chlorite, as reported by Heath et al. (2010).

213 Kirtland Shale synthetic brine composition (g/L) is: NaCl: 17.0; KCl: 0.295; magnesium chloride (MgCl₂): 0.075.

214 Eau Claire synthetic brine composition (g/L) is: NaCl: 93.174; KCl: 2.137; CaCl₂: 39.366; MgCl₂: 8.495; MgSO₄: 1.695; NaHCO₃: 0.145.

215 Tuscaloosa synthetic brine composition (g/L) is: NaCl: 109.63; KCl: 0.60; CaCl₂: 32.40; MgCl₂: 4.13; sodium bromide (NaBr): 0.53; strontium dichloride (SrCl₂): 1.248.

216 The resulting flow rate was approximately 6.9 x 10⁻⁴ mL/min.
- The permeability of the sample did not change appreciably over the 25-day course of the experiment, based on flow rate observations.

- Little change in the aperture was noted over the period (however, note the low flow rate).

- Geochemical changes were noted in the brine in the test (Figure D5), with significant decreases in Mn and Nickel (Ni), and a significant increase in Sr. There were also increases in Si, S, Na, Ca, copper (Cu), and K, and decreases in Mg and titanium (Ti).

![Fractured Kirtland Brine Pre/Post Chemical Analysis](image)

Source: Crandall and Bromhal (2014)

Notes:

a Results of flow-through tests with naturally-fractured Kirtland Shale, San Juan Basin, New Mexico.

b The sample was tested with CO₂-saturated brine for 25 days using a constant injection pressure of 11.17 MPa, a controlled temperature of 27 °C, and a confining pressure of 12.76 MPa. Little change in permeability was noted during testing.

Figure D5: Changes in geochemistry in fractured Kirtland Shale during a flow-through test by Crandall and Bromhal (2014).

Results of the testing with the two Eau Claire samples indicated:

- In both samples, no conclusive changes in the fracture due to the brine exposure were observed based on the medical CT images.

- In both tests, while the bulk dual-energy density was variable, no significant changes were noted over the duration of the test (19 to 22 days).
• In Sample #1, the fracture showed zero aperture zones (i.e., regions where the fracture walls are in contact).

Results of the testing with the Tuscaloosa sample indicated:

• No significant changes in the bulk dual-energy density were noted over the duration of the test (39 days).
• The pressure differential pressure for flow increased from about 22 kPa (3.3 psi) to about 30 kPa (4.4 psi) over the duration of the test, indicating a decrease in permeability (and hydraulic aperture) of the fracture with time.

Edlmann et al. (2013) tested two fractured mudstone samples and one intact sample exposed to scCO₂ and gaseous CO₂ flow to evaluate the sealing capacity of the rock.

The three test samples were from the Kimmeridge clay unit taken from the North Sea East Brae oil and gas field on the western margin of the South Viking Graben. The tested core was from an Upper Jurassic Formation and taken at a depth of 3,910 to 3,918 m. The three samples (labeled here as A, B, and C) had little carbonate content (about 1.5%) and a clay content of approximately 46% (composed of illite: 28.7%; kaolinite 7.6%; chlorite 7.6%; muscovite 2.2%) based on the testing of the Sample A matrix. Testing of the sample fracture indicated a slightly higher carbonate content (about 5%) and a reduced clay content of about 42%.

Samples A and B both contained a visible, throughgoing, natural longitudinal fracture networks. The third sample, Sample C, appeared intact and testing was intended to measure matrix flow alone. The sizes of the three samples varied somewhat, with all samples having similar diameters but varying lengths. Sample A had a diameter of 38.1 mm, and a length of 49.6 mm, Sample B had a diameter of 37.9 mm and length of 54.1, and Sample C had a diameter of 38.1 mm and length of 60.5 mm.

A synthetic brine was prepared for testing by mixing m 1 L of 58,000 NaCl eq. ppm and 40 g of crushed rock prepared for 2 months at 25 °C and then filtered. The samples were vacuum saturated in this brine for 4 weeks and then placed into a Hassler-type high-pressure vessel, and a series of test phases were conducted.

For the fractured samples, the test consisted of three phases which were repeated for a total of two cycles in the test program:

1. Phase 1 involved the flow of scCO₂ with an increasing upstream fluid pressure from 10 to 40 MPa (concurrently increasing confining pressure from 20 to about 55 MPa) over a period of one day at a temperature of 40 °C and a constant upstream pressure of about 0 MPa.

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217 Approximately halfway between Kirkwall, Scotland (Orkney Islands) and Stavanger, Norway.
218 The confining pressure was maintained at between 5 and 20 MPa above the fluid pressure.
2. The second phase involved scCO₂ with a constant upstream fluid pressure of 10 MPa, and a constant confining pressure of 25 MPa, over a period of 29 days at a temperature of 40 °C and a constant upstream pressure of about 0 MPa.

3. The third phase involved gaseous CO₂ with a constant upstream fluid pressure of 5 MPa, a constant confining pressure of 20 MPa, but with an increasing downstream pressure from 0 to 5 MPa, over a period of 30 days at a temperature of 20 °C.

The results of the test program were:

- During the variable pressure conditions in Phase 1, there was no detectable flow of scCO₂ for both samples.
- During the constant conditions of Phase 2, there was little or no detectable scCO₂ flow for both samples.
- Upon initiating Phase 3 with gaseous CO₂, the downstream pressure started to increase steadily to the upstream pressure over the period of 30 days, indicating flow through the rock.
- For the intact sample, data from the “three-phase then repeat” test program indicated “no quantifiable flow measurement” across the intact sample under either scCO₂ or gas CO₂ phases of testing.
- The elemental testing of Sample A indicated that there was a slight reduction in Si (2%) content and a corresponding increase in Al content (2%) after exposure to CO₂ in both the matrix and the fracture. Data also indicated increases in Mg and Ca along the fracture but not in the matrix. Further, there was a minor increase in Fe in the matrix but not the fracture.
- No evidence of swelling was observed based on sample dimensions before and after testing and the lack of volume changes during testing.

The authors indicated that contrary to observed data, it was expected that scCO₂ should have penetrated the rock fracture more readily than gaseous CO₂ given the lower diffusivity of scCO₂. The authors concluded that observed result could have been caused by experimental error, or more likely, that it was due to the complex interplay of the various factors influencing the flow of CO₂ along a fracture. The authors provided an extensive discussion on this topic (which is not repeated here).

The authors mention the following factors as affecting CO₂ flow through fractures:

- The influence of normal effective stress across the fracture and the stress/pore pressure gradient along the fracture.
- Chemistry influence on the fluid/rock mineralogy interaction.
- Fluid pressure influence on permeability.
- Influence of CO₂ phase on capillary entry pressure.
- Influence of CO₂ phase on the interplay between interfacial tension, contact angle, and wettability.
- Fluid conductivity response of the CO$_2$ phase to fracture aperture, tortuosity, and roughness.

Smith et al. (2013) conducted a flow test on a fractured greywacke sample at elevated temperature and pressure. The sample was taken from a surface outcrop near the Ohaaki-Broadlands geothermal field, northeast of Taupo, New Zealand. The local greywacke is typically described by other authors (e.g., Wood et al., 2001) as: “rich in quartz and feldspar minerals, argillite, chlorite stringers, and locally variable quantities of epidote and/or calcite, as well as trace illite, pyrite, muscovite, and secondary K-feldspar.” The sample was specially cored from a rock block to ensure that a natural fracture roughly bisected the test sample’s long axis. After coring, the fracture was opened, inspected and then closed/mated.

The test sample (15 mm diameter and 30 mm height) was wrapped with a fluoropolymer heat-shrink material and tested in a reaction vessel with a core-flooding setup. Initially, the sample was pressurized to a confining pressure of 25 MPa at room temperature and permeability tests were performed with a saline solution (0.05 M NaCl) at varying pore pressure/confining pressure ratios. The sample was then heated to 200 °C and the sample was injected with the saline solution (alone) at a constant flow rate for 2 weeks to stabilize the sample. The inlet flow rate was maintained at 0.01 mL/min, with an outlet pressure of 8.3 MPa. After this aging period, the sample was subjected to a CO$_2$ saturated brine (5.5 MPa partial pressure of CO$_2$), injected at a constant flow for the next 49 days.

From the authors, the major test results were:

- The permeability of the sample increased during the entire test period. The differential pressure across sample decreased continuously and significantly both during the initial 14-day period with brine alone and over the longer period subjected to brine-CO$_2$. The differential pressure declined from about 7 MPa to about 0.3 MPa over the 63-day period.

- Substantial evidence of both dissolution and secondary mineral precipitation were observed in the sample at the end of the test.

- Imaging revealed the existence of a fully-throughgoing dissolution channel along the fracture, which developed during testing, but this channel was generally isolated from other pre-existing larger spaces along the fracture. Away from this dissolution channel, fracture apertures (of larger size) appeared to have decreased, indicating mineral precipitation in isolated, larger, off-channel regions.

- Changes in the saturation index of representative minerals are shown in Figure D6. Representative clay minerals of kaolinite and paragonite, which exhibited high saturation index values (i.e., were supersaturated) during the period of brine-only flow, show decreasing saturation index values with time after the introduction of CO$_2$. After day 20, these values approached equilibria and were essentially constant. The remaining four minerals (barite, quartz, calcite and sodium feldspar) show some initial variability and a small decrease, but then the saturation indices become also essentially constant for days 10 to 32. At day 32, four of the minerals of the six minerals show a jump in the saturation index values and then decrease, possibly due to a short period of depressurization at about day 30.
- From dissolved concentrations in the brine versus time, the concentrations of Mg, Ca, Ba and SO₄ show a major jump upon introduction of CO₂, but then decrease sharply to a steady-state value with time. In contrast, the concentration Si increases over the entire period, increasing about an order of magnitude in 49 days. The metals, Fe and Al, show highly variable concentrations with time (perhaps a somewhat cyclic variation with time).

- Particle image velocimetry data indicated a net movement toward the fracture plane, with fracture aperture reduction greatest in the competent areas not experiencing fracture surface dissolution. The method also identified the three-dimensional rotation of particles or grains liberated by dissolution.

![Diagram showing changes in mineral saturation indices due to CO₂ exposure](image)

Source: Modified from Smith et al. (2013)

Notes:

a Results of core flood test with a fractured greywacke from the Ohaaki-Broadlands geothermal field in New Zealand. Only the CO₂ exposure portion of the test is shown in the figure.

b The sample was tested with CO₂-saturated brine for 49 days at 200 °C at a constant injection rate.

c The authors stated that the increase in saturation indices for several phases at durations greater than 30 days may be related to a short depressurization event at 29.9 days in which upstream/inlet pressures decreased below that of the back pressure regulator.

d If the Saturation Index is equal to zero (i.e., log Q/K = 0), the reaction is at equilibrium. K = equilibrium constant for the reaction; Q = reaction quotient.

Figure D6: Changes in mineral saturation indices due to CO₂ exposure during a core flooding test at 200 °C by Smith et al. (2013).
Kumar (2014) and Kumar et al. (2016) conducted flow tests on intact and fractured flow tests on shale samples from Pennsylvania. Permeability tests on two intact samples were first conducted and are discussed earlier (Appendix B.2.1). After intact permeability testing, one sample was cut in half using a thin diamond coated blade. This sample was then reassembled and tested as is (clean fracture), and then subsequently, the same sample was tested with a single uniform layer of proppant on the fracture.

The source formation(s) of the samples was not mentioned. Two samples were taken from a larger rock block (samples A and B) and were cored parallel to bedding. Test samples were prepared as cylinders, 2.5 cm in diameter and 5 cm in length. The clay content or type of clay minerals in these samples was not noted. The porosity of Sample A was 34%, in contrast to a porosity of 5% for Sample B.

In more detail, after initial permeability testing, Sample A was cut in half (axially) using a thin diamond coated blade to produce smooth opposing surfaces. The sample was first tested with a clean fracture. The fracture was then filled with a proppant and tested again. For the propped phase of testing, the fracture was coated with a uniform monolayer of #70-140 mesh\textsuperscript{219} proppant sand to test the influence of propped fractures on permeability evolution. The core was wrapped in aluminum foil to prevent any adsorption or diffusion of CO\textsubscript{2} through the rubber jacket during the permeability experiments.

The samples were tested in a triaxial cell at a confining stress of 10 MPa, using a transient pulse test method to determine gas permeability with both He and CO\textsubscript{2}. The temperature for testing was held constant, but a specific test temperature was not mentioned (other tests were conducted at room temperature, approximately 20 °C). The gas pressure in the tests ranged from approximately 1 MPa to 6 MPa. Samples were first tested with He and then with CO\textsubscript{2} gas.

Results from permeability testing are shown in Figure D7. The clean fracture shows more than a two-fold increase in permeability with increasing pore pressure from 1 to about 5 MPa. Testing with He evidenced a more gradual, increase of about a 30% over the same gas pressure range trending in a linear fashion. The final permeability of the clean (unpropped) fracture was roughly 10 mD of both He and CO\textsubscript{2} tests at 5 MPa.

Testing with He on the propped fracture again showed an increase in permeability with gas pressure, going from about 13 mD to 31 mD at 5.5 MPa. However, testing of the propped fracture with CO\textsubscript{2} showed a significant decrease in permeability with increasing pressure, decreasing from about 20 mD to 10 mD over 1 MPa to 5 MPa range (see Figure D7).

\textsuperscript{219} Based on ASTM E 11-16 (ASTM, 2016), the specified opening dimension (i.e., the opening dimension exceeded by not more than 5%) of the US #70 mesh is 242 µm, and the #140 is 126 µm. The predominate range of particles is typically considered to be 106 µm to 212 µm (e.g., Horiba Scientific, 2017).
Notes:

Testing with shale Sample A (formation unknown). In Phase 1, the sample was tested with CO₂ gas along a clean, artificial (saw-cut) fracture. In the second phase of the test, the fracture was propped with a single layer of #70-140 proppant. Test temperature(s) are not known.

Figure D7: CO₂ gas permeability results on artificial and propped fractures in shale by Kumar (2014).

Scans using white light optical profilometry indicated surface changes on the propped surface comparing at before and after testing. The surface roughness changed from 4.1 μm pre-testing to 6.1 μm post-testing and the peak to valley differential surface increased from 77.9 μm to 122.4 μm. The authors concluded that the proppant particles indented the surface with the applied pressure, creating small pits and increasing the apparent roughness values.
Deep and wide interconnected pores were observed uniformly distributed on the fracture surface.220

No time-dependent reactions were noted during this testing (although He/CO₂ cycling during permeability testing of intact specimens did indicate some reduction of permeability). In addition, the authors discuss the similarities of the CO₂-shale response to that of CO₂ with coal and provide a theoretical model for their concepts.

Carey et al. (2015) conducted 16 experiments on Utica Shale samples in both compression and direct shear while simultaneously measuring permeability. Only four of the compression experiments were conducted with scCO₂.

The samples of Utica Shale tested with scCO₂ (i.e., samples labeled RU-6964, RU-6840, MG-5878 and KB-8440) were from boreholes in Ohio and Pennsylvania at depths ranging from 1,700 to 2,700 m. As noted by the authors, some samples were distinctly layered with carbonate/fossil accumulations. The carbonate contents of the four samples (termed here as the “designated samples”) were high, ranging from 49.3% to 79.3%, and the clay content rather small, ranging from 6.4% to 17.1%. Most of the 16 samples of the program were stored at “lab” conditions so that they were only partially water-saturated prior to testing.

The experiments were conducted in a triaxial core-flood system coupled with an X-ray tomography unit. The four designated samples were tested at 45 °C and 11.7 MPa confining pressure. Bedding of all four designated samples was oriented perpendicular to the applied axial load (termed horizontal orientation). Samples were cylindrical in shape, 2.5 cm in diameter, and with a sample height of roughly 2.5 cm (having approximately a 1:1 height to diameter ratio).

The test system was instrumented to measure piston displacement, axial and radial sample strain, temperature, and acoustic properties of samples. After preparation, samples were placed in the triaxial cell, pressurized and then heated to the specified test temperature. The samples were then subjected to an increasing axial load at a constant strain rate of about approximately 10 micro-strains per second. The samples were also subjected to a constant flow rate with a differential pressure across the core of greater than 1.4 MPa.

Test results of this test program indicated that compression experiments typically showed approximately linear elastic behavior up to a distinct failure event followed by moderately-ductile strain softening. For all tests, horizontally-oriented samples evidenced increased

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220 It should also be observed that the proppant can enhance and modify flow channels on the fracture surface and increase the surface area exposed to CO₂ reactions due to penetration.

221 It is supposed that the 4-digit numbers of each sample refer to depth of sampling in feet.

222 The mineralogy for only three of the four designated samples was reported: RU-6964, MG-5878 and KB-8440, with sample MG-5878 having the highest carbonate content and lowest clay mineral content of the three, and KB-8440 having the lowest carbonate content and the highest clay content.

223 Samples were stored at 20 °C and in open air, or in otherwise uncontrolled indoor conditions.

224 Specific flow rates not discussed; from figure in paper, flow rates were on the order of 1 to 10 mL/min.
strain at failure, with the designated samples having axial strains of 0.055 to 0.0290 at yield. The peak stress at failure for the four samples ranged from 52.7 MPa to 88.9 MPa.

All samples had a non-measurable permeability (i.e., less than 0.001 mD) at the start of testing. The permeability of the samples in compression typically increased up to yield and then decreased thereafter. The maximum permeability of the designated samples ranged from 0.1 mD to 0.27 mD, and these values were smaller than the permeability of other samples in tested in compression with water. In comparison, the maximum effective permeability of samples tested in direct shear with water showed permeabilities of several hundred mD up to 900 mD. No alteration, time-dependent or other concerns from using scCO₂ were reported by the authors.

Further, the authors provided an extensive discussion and analysis on fracture development and displacement in direct shear. They concluded that the shear activation of existing fracture systems is most likely the source of permeability in shale plays given the amount of deformation that would be required to form new fracture networks.

Li (2016) and Li et al. (2016) performed several permeability tests on fractured shale samples using proppants with CH₄, CO₂, N₂, and He gases at various pore pressure. Tests were conducted on samples from the Green River Shale Formation. The source and depth of the rock were not discussed. In addition, the mineralogy, the orientation of bedding to the fracture, proppant packing, initial water content and sample storage conditions were also not discussed by the authors.

Permeability tests were conducted on 1-in. diameter and 2-in. high samples, which were axially split to provide a fracture. The fracture surfaces were polished and then coated with a single layer (monolayer sample) or four layers (polylayer sampler) of CARBOLITE 40/80\textsuperscript{225} mesh proppant, and then the two halves were re-assembled.

The pulse method was used to conduct gas flow experiments in a triaxial pressure cell. All tests were conducted at constant confining of 20 MPa and an axial stress of 10 MPa, at room temperature of about 25 °C. The downstream pressure was maintained at approximately 1.0 MPa lower than the upstream pressure. For each test, He was injected first at varying gas pressure, then cycled down to the initial pressure; this was followed by testing with (in order) N₂, CH₄ and then CO₂ with the same fracture.

Results from the testing are:

- Testing of propped monolayer fractures with the adsorptive gases (i.e., CO₂, N₂, and CH₄) initially exhibit a trend of decreasing permeability with increasing gas pressure, as shown in Figure D8. At pressures greater than 7 MPa, permeability values become constant and seem to suggest a trend of increasing permeability (with increasing pressure) at higher pressures. In contrast, He (considered non-absorptive) shows a trend of increasing permeability with increasing pressure for the entire pressure range.

\textsuperscript{225} CARBOLITE is a high-performance, low-density ceramic proppant (CARBO, 2017).
• Testing of a polylayer (four layers of proppant) sample and a monolayer (single-layer of proppant) sample with CO₂ yielded similar permeability results in both value and trends, with the polylayer sample exhibiting slightly larger values at the same gas pressure (Li, 2016).

• The short duration of gas exposure did not have a significant influence on permeability for both adsorptive or non-adsorptive gases with the samples. Permeability testing of a monolayer samples exposed to either CO₂ or He over a period of 20 to 22 hours showed no apparent change in permeability (Li, 2016).

• Surface scans for roughness indicated that the initial clean fracture sample was the smoothest type with no embedment effect, based on parameter analysis. From the data, the monolayer surface appeared to be the roughest (i.e., more than the polylayer surface).

Figure D8: Gas permeability results on artificial, monolayer-propped fractures in shale by Li (2016).

Notes:

a Gas testing on Green River Shale with artificial (split) fracture propped with a single layer of 40/80 ceramic proppant, at a confining pressure of 20 MPa and at room temperature (about 25 °C).

b The original figure was digitized and permeability values converted to mD.
• Testing of three monolayer samples exposed to CO₂ show some variability in absolute results but all exhibit similar trends of permeability versus gas pressure. At a gas pressure of about 2 MPa, permeability values of approximately \(3.8 \text{ m}^2\), \(2.6 \text{ m}^2\) and \(2.5 \times 10^{-15} \text{ m}^2\) were measured for three samples, labeled B, A and C, respectively. Variation above 8 MPa was significantly smaller with differences less than \(0.5 \times 10^{-15} \text{ m}^2\) (Li, 2016, Figure 3.10).

• Permeability values from injection and depletion cycles generally were repeatable, and show little hysteresis.

van Noort and Yarushina (2016a)\(^{226}\) performed multiple permeability tests on a single shale sample using water and scCO₂. The single sample was cored at a depth of 375.25 m to 375.47 m in the Adventdalen Valley on the island of Spitsbergen (part of the Norwegian Svalbard archipelago), near Longyearbyen. The unit was assessed to be from the Rurikfjellet Formation, and from XRD analysis of a sample from a nearby boring, the unit is primarily composed of illite, with only minor interlayered smectite, quartz, and plagioclase, with minor carbonates, kaolinite, and Fe-chlorite. The sample plug was drilled parallel to bedding.

For this test program, the cylindrical sample had a diameter of 25 mm and a height of 10 mm. The sample was tested in 5 phases, with the first four phases using water as a permeant, and only using scCO₂ in the final, fifth phase. The division of the test phases with water was based on the need to remove the core from the sample jacket due to leakage during the testing. The jacket was also removed before scCO₂ testing to place aluminum foil on the exterior of the sample to limit flow through the sample membrane.

The nature of the sample was altered during testing. The sample was originally intact, but during the first jacket removal (i.e., at the end of Phase 1), the sample fractured longitudinally along the sample axis and was tested as is.\(^{227}\) Phases 2 to 5 were therefore conducted on a fractured core.

The transient pulse method was used to conduct permeability experiments within a pressure cell. For each test cycle, the confining and pore fluid pressures are increased stepwise, with measurements taken after reaching the specified test conditions after system stabilization. For the interval between Phases 4 and 5, the sample was flushed with supercritical CO₂ and air-dried to remove pore water and prevent two-phase flow effects.

For the first four phases (using water), the confining pressure was varied during each phase, ranging overall from 4 to 25 MPa. The temperature was also varied with Phase 1 and 2 at room temperature (23 °C to 25 °C) and Phase 3 and 4 conducted at 40 °C. The initial pore pressure was also varied, ranging from 2.5 to 7.5 MPa. In contrast, the fifth test phase with scCO₂ was conducted at constant confining pressure 25 MPa, a pore pressure of 7.5 MPa and

\(^{226}\) Permeability results are also briefly described by van Noort and Yarushina (2016b), which appear to be similar to the current reference.

\(^{227}\) The fracture did not appear to be along a bedding plane as no distinct bedding plane was evident in the photograph provided by the authors.
at a constant 40 °C temperature. Three separate test cycles were conducted as part of this test phase, with the sample remaining pressurized between cycles.

Test results indicated the following:

- Testing in Phase 1 with water indicated that permeability decreased with increasing effective confining pressure, and the original permeability was not recovered upon unloading, indicating that the decrease was due to compaction of the intact specimen or sealing of the fracture. The permeability of the intact sample under Phase 1 varied from $6.6 \times 10^{-18}$ m$^2$ to $2.4 \times 10^{-20}$ m$^2$ at room temperature. (The curve resembled the strain hardening response of a normally consolidated clay under loading and load reversal.)

- During the second phase of testing with water, permeabilities of $1.9 \times 10^{-19}$ m$^2$ to $2.0 \times 10^{-21}$ m$^2$ were obtained, which are similar or lower than the values obtained for the intact sample. The comparable values suggest that the fracture mostly closed at higher effective stresses in this phase.

- The third phase was conducted with water at a higher temperature, indicated permeability values of $9.6 \times 10^{-22}$ m$^2$ to $2.3 \times 10^{-21}$ m$^2$. The values suggest a limited impact of increased temperature on permeability with water.

- Testing with scCO$_2$ evidenced decreasing permeability with each successive cycle or measurement. The initial permeability with scCO$_2$ was $1.6 \times 10^{-20}$ m$^2$. The permeability of the second cycle indicated a value of $3.2 \times 10^{-21}$ m$^2$, with the third value of $1.4 \times 10^{-21}$ m$^2$. The second permeability value was comparable to that obtained with water prior to CO$_2$ testing. The authors discussed several possible causes for the decreasing trend with increased testing including sample disturbance due to sample handling and re-jacketing.

D.2.4. **OTHER TESTS WITH CO$_2$**

Other tests involving CO$_2$ and shale include surface reaction tests and hydraulic fracturing tests. These types of experiments were conducted by Shao et al. (2010) and Zhou et al. (2016), and are summarized in the following sections:

**Shao et al. (2010)** conducted experiments with phlogopite to investigate dissolution kinetics and surface morphology at elevated temperature and pressure. Phlogopite is reddish-brown mica (also known as magnesium mica) and was used as a representative clay mineral in the test program. The sample was obtained from Ward’s Natural Science, NY, with the original source in Ontario, Canada (Wards, 2017; Vali et al., 1992). For testing, phlogopite crystals were cleaved to thin samples (about 20 µm thick), and cut into a rectangular shape of about 2.5 cm x 0.8 cm. The surface was cleaned with water, acetone, ethanol, and isopropyl alcohol to remove organic matter.

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228 The order of magnitude shown is based on authors’ discussion of results and their figure; the first value shown in table for scCO$_2$ is apparently in error.
Tests were conducted at a pressure of 10.3 MPa and a temperature of 95 °C using a benchtop reactor. CO2 was injected into a solution of 1 M NaCl under pressure to create a synthetic brine for exposure. The samples were then exposed to the CO2-brine, and the reacted fluid was periodically sampled over the test duration of 159 hours.

Monitoring data from the tests showed a marked increase in K in solution, increasing to approximately a concentration of 800 µM at 159 hours. In contrast, Si and Mg showed only minor increases in concentration, with both values of about 80 µM at test end. Al showed little change with a final value of about 10 µM. The rate of concentration increase for all constituents was essentially linear over the test duration. The same test but performed with N2 indicated that observed dissolution concentrations of different elements were less than 10% of those under CO2, except for K.

Examination of the sample surface during CO2 exposure showed the creation of dissolution pits and the existence of nanoscale precipitates on surfaces. The dissolution effects started as isolated shallow pits on the surface at the beginning of the test, but as the reaction proceeded, the pits became deeper and larger, connecting with other pits and in cases forming channel-like structures. In addition, contrary to the authors’ expectation, the formation of nanoparticles on the surface was observed after only 5 hours of exposure. The significantly different colors of these newly formed particles indicated that the nanoparticles were a secondary mineral phase(s).

The authors observed a specific sequence in the dissolution/precipitation process as illustrated in Figure D9. Initially, secondary mineral deposits formed near the edges of dissolution pits. A few hours later, the pits grew wider and deeper, but the secondary deposits (which were also growing) inhibited the dissolution of the underlying phlogopite mineral, thereby leaving the deposits that were entirely enclosed within the pits. With time, each of the separate secondary deposits was isolated, then completed undermined by dissolution; during the final stage, the deposits separated and migrated from the original location, and collected elsewhere downflow.

Also of note, when the phlogopite sample was washed after the test, the secondary deposits remained on the surface, suggesting that the secondary mineral phases had a greater affinity for the phlogopite surface than for the brine-CO2 solution, a behavior which was consistent with the observed process.

Identification of the secondary minerals proved problematic, but the authors surmised that most of the secondary mineral phase was amorphous silica. They also concluded that these secondary mineral coating could alter the wettability of the surface and impact permeability of a fracture.
Notes:

- Proposed sequence of reactions on phlogopite surface exposed to CO₂-brine over a period of 5 hours to 22 hours after the start of the test. The black areas represent the formation of secondary minerals.
- The sequence is within a near-surface zone, where concentrations and pH are higher than in the bulk solution.
- The final pit depth was up to 15 μm.
- Not to scale.

Figure D9: Timeline schematic of proposed for dissolution and precipitation reactions on phlogopite surface by Shao et al. (2010).

**Zhou et al. (2016)** hydraulically-fractured three shale samples and then subsequently conducted gas permeability tests on these samples using scCO₂.

The samples were from an outcrop of the Longmaxi Formation of the Lower Silurian in the Sichuan Basin, obtained in the Changning region near Yibin City, China. The samples had a clay content of approximately 20.1% and a carbonate content of 31.0%. The TOC was about 4.18%. Samples were cored perpendicular to bedding.

The samples of the program were cylindrical, 100 mm in diameter and 200 mm in height, with a central hole (8 mm diameter) drilled axially (Figure D10).
A special hydraulic fracturing test apparatus was developed for fracturing the samples, as described by the authors. Samples were sealed using heat shrink tubing and then inserted into a triaxial cell. Each sample was fractured at a confining pressure ($\sigma_2$) of 15 MPa, an axial stress ($\sigma_1$) of 20 MPa, and at a constant fluid injection rate of 30 mL/min of scCO$_2$. The test temperature was maintained at 35 °C. After fracture completion, permeability tests were conducted over a range of confining pressures of about 2 to 10.5 MPa under a constant gas injection pressure of 4 MPa. These tests were conducted with He, N$_2$, and CO$_2$ gases.

For the fracturing process, a pipe tipped with a porous disk was inserted into the central hole and sealed (epoxied); the system was then pressurized to failure. During testing, the samples were monitored for acoustic emissions and axial deformation, and before and after testing, the exterior surface was photographed by a high-definition camera and the sample itself was characterized with CT scanning. After completing the hydraulic fracturing phase, the steady-state permeability of the sample was measured, assuming Darcy’s law. Three samples were tested in the program. Preparation details, water content, and storage conditions of the samples were not discussed.

From test data, the scCO$_2$ breakdown pressure measured in the three samples evidenced some variability, with pressure values of 7.6, 11.9 and 14.0 MPa. The authors noted that these pressures were lower than that typically obtained by fracturing with water. From the figures provided, the pressure-time curves were typical of the fracturing process.

The fractures generated in the samples by hydraulic fracturing were observed to be complex, with several branches and oriented in different directions, both parallel and perpendicular to bedding. The fractures were generated primarily in shear, but tensile fractures were observed as well.
The authors also indicated that the fracture extension model with scCO₂ appeared to be different from that of water, with fractures extending deeper into the rock matrix itself, into smaller pore spaces and microfractures. This was attributed to the high diffusivity, low viscosity, and low surface tension of scCO₂ compared to water. The authors also mentioned the displacement of CH₄ by CO₂ by de-adsorption/sorption in the rock.

Permeability testing evidenced that the fracture system permeability decreased with increasing effective stress for all three gases and that the measured permeability varied with the gas type used in testing (Figure D11). The permeability with He was observed to be greater than with N₂, which in turn was greater than with CO₂. The decrease was attributed to the increasing sorption of the respective gases (i.e., CO₂ has the lowest permeability and has the highest sorption).

The authors also indicated that measured permeability depended on the stress path based on pressure cycling with He and N₂. The permeability is reduced dramatically when the effective stress increase is caused by the increase of the confining pressure, whereas it decreases slowly when the effective stress increase is caused by the decrease of the pore pressure.

Source: Zhou et al. (2016)

Notes:

a) Samples were from the Longmaxi Formation in China and fractured by hydraulic fracturing of samples.

b) Samples were 100 mm in diameter and 200 mm in height, with a central hole.

Figure D11: Variation in gas permeability of fractured shale versus effective stress by Zhou et al. (2016).