Review of the Effects of CO₂ on Very-Fine-Grained Sedimentary Rock/Shale – Part I: Problem Definition

3 June 2016

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Cover Illustration: Stylized figure depicting the flow of supercritical CO₂ 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 Évelyne 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 I: Problem Definition

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<thead>
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<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Activity</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon capture, and storage</td>
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<tr>
<td>CEC</td>
<td>Cation exchange capacity</td>
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<tr>
<td>CH₄</td>
<td>Methane</td>
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<tr>
<td>CO</td>
<td>Carbon monoxide</td>
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<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
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<tr>
<td>CPG</td>
<td>CO₂-plume geothermal</td>
</tr>
<tr>
<td>DOE</td>
<td>U.S. Department of Energy</td>
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<tr>
<td>EGR</td>
<td>Enhanced gas recovery</td>
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<td>EOR</td>
<td>Enhanced oil recovery</td>
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<tr>
<td>H₂O</td>
<td>Water</td>
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<tr>
<td>H₂S</td>
<td>Hydrogen sulfide</td>
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<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>ISRM</td>
<td>International Society of Rock Mechanics</td>
</tr>
<tr>
<td>LL</td>
<td>(Atterberg) liquid limit</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>NETL</td>
<td>National Energy Technology Laboratory</td>
</tr>
<tr>
<td>PI</td>
<td>Plasticity index (PI = LL-PL)</td>
</tr>
<tr>
<td>PL</td>
<td>(Atterberg) plastic limit</td>
</tr>
<tr>
<td>PS</td>
<td>Point load strength</td>
</tr>
<tr>
<td>Rₚ</td>
<td>Shale Rating System Value (Franklin, 1981)</td>
</tr>
<tr>
<td>RIC</td>
<td>Research and Innovation Center</td>
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<tr>
<td>scCO₂</td>
<td>Supercritical carbon dioxide</td>
</tr>
<tr>
<td>SD</td>
<td>Slake durability index</td>
</tr>
<tr>
<td>SL</td>
<td>(Atterberg) shrinkage limit</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solids</td>
</tr>
<tr>
<td>USCS</td>
<td>Unified Soil Classification System</td>
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Acronyms, Abbreviations, Symbols (cont.)

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<th>Abbreviation</th>
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<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>GPa</td>
<td>Gigapascal ((10^9 \text{ Pa}))</td>
</tr>
<tr>
<td>kg</td>
<td>Kilogram ((10^3 \text{ g}))</td>
</tr>
<tr>
<td>km</td>
<td>Kilometer ((10^3 \text{ m}))</td>
</tr>
<tr>
<td>kPa</td>
<td>Kilopascal ((10^3 \text{ Pa}))</td>
</tr>
<tr>
<td>m</td>
<td>Meter</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeter ((10^{-3} \text{ m}))</td>
</tr>
<tr>
<td>μm</td>
<td>Micrometer, micron ((10^{-6} \text{ m}))</td>
</tr>
<tr>
<td>ηm</td>
<td>Nanometer ((10^{-9} \text{ m}))</td>
</tr>
<tr>
<td>MPa</td>
<td>Megapascal ((10^6 \text{ Pa}))</td>
</tr>
<tr>
<td>Pa</td>
<td>Pascal</td>
</tr>
<tr>
<td>psi</td>
<td>Pounds per square inch</td>
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Acknowledgments

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EXECUTIVE SUMMARY

Carbon dioxide (CO₂) occurs naturally underground and currently is also being employed in a number of industrial subsurface applications. A comprehensive study was initiated to review the potential effects of the flow of carbon dioxide on very-fine-grained sedimentary rock, in particular, shale, as reported in the literature. An emphasis of the study is to characterize the potential of the shale to swell when exposed to CO₂, and how to identify the potential for swell when used at a specific site.

This report is the first in a sequence of progress reports from this study and provides a basis for subsequent reports. This report describes some of the major industrial processes that utilize CO₂ in subsurface applications, and then examines the term “shale” as used as a basis for this research. Note that the term, shale, while being used for hundreds of years, is highly ambiguous and is used differently by various technical disciplines.

Major summary points of the report are:

1. CO₂ is currently being used in a variety of subsurface activities over a range of in situ conditions. Additional activities are under study. All of these activities can give rise to complex interactions of CO₂, in situ fluids and the rock mass.

2. “Shale” is a term that is widely used in various fields, yet poorly defined in a scientific sense. A clear definition of the actual shale material used in any research project should be fundamental to project reporting, including a detailed description of the overall mineralogy, the amount of clay minerals, and the type of clay minerals.

3. The macrofabric of shale is important to understanding behavior for any process, yet is rarely considered. The microfabric is also rarely described in detail in the literature.

4. A revised definition of shale is proposed for carbon capture and storage (CCS) community interested in quantifying shale and CO₂ interactions.
1. **INTRODUCTION**

1.1 **SCOPE**

This report is part of a sequence of reports that reviews the current state of knowledge on the response of very-fine-grained sedimentary rocks to the flow of supercritical carbon dioxide (scCO₂) and brine. In particular, this multi-part review focuses on the potential for rock expansion and contraction (typically stated as rock swell) of shales as well as other effects that can change fracture aperture, affect fluid flow and affect rock properties important for captured carbon storage and enhanced geothermal systems.

This document provides a basis for the reviews in subsequent reports. This report first discusses the industrial and environmental processes that currently use (or propose to use) carbon dioxide (CO₂) in the subsurface. This discussion is used to establish the subsurface pressures and temperatures for describing CO₂ behavior. The next section examines differing classification approaches to provide a clear definition of shale and address ambiguities in the literature.

1.2 **PROBLEM STATEMENT**

CO₂ exists naturally in the subsurface, together with other gases such as carbon monoxide (CO), methane (CH₄), hydrogen sulfide (H₂S), and noble gases. In addition, in recent years, CO₂ has been injected in the subsurface for the purposes of enhancing hydrocarbon recovery and for geothermal energy production, and is also being studied for storage at depth to address issues of climate warming. As all these efforts are often conducted at substantial depths in saline environments, the resulting fluid is actually a combination of scCO₂ and brine, with some dissolution of the CO₂ into the brine. As scCO₂ is less dense than the native brine, after injection, there is a natural flow upwards, passing through the more-permeable injection horizon (say a sandstone or limestone unit) until encountering a less-permeable horizon, often identified as a caprock or seal shale.

The flow through the caprock can have significant consequences. For CO₂ sequestration, the caprock is intended to limit the upward CO₂ flow into the biosphere as much as possible. This flow is actually a dynamic process, as the scCO₂-brine is expected to interact with the caprock which will influence the transmissibility of the material system. For some factors, the physiochemical reactions may increase the transmissibility, while other factors may substantially reduce the flow. This also pertains to applications where the formation is used to store scCO₂.

The present report examines the current literature to identify the possible range of expected effects of the scCO₂-brine fluid on shale rock masses. As there is limited information on the topic, the search scope includes summarizing the effects of other fluids on shale response. As “shale” is not a well-defined term, the methods used to identify shale are also briefly examined. In all these areas, the techniques and approaches are critically examined, identifying limitations and making recommendations to address these issues.
2. **PROCESS DESCRIPTION – SUBSURFACE USES OF CO$_2$**

2.1 **SEQUESTRATION IN GEOLOGIC MEDIA**

As noted by the scientific community at large (e.g., Shukla, 2010; Edlmann et al., 2013), there has been a major increase in the atmospheric concentration of CO$_2$ and other related greenhouse gases since the start of the industrial revolution, and various efforts are being studied to stabilize the CO$_2$ level in the atmosphere. One approach is to store (sequester) the CO$_2$ at depth in geologic media, which can be achieved by various approaches. These approaches include (Bachu, 2000, Jones and Blondes, 2015): (1) injecting CO$_2$ into deep saline (non-potable) rock units; (2) injecting CO$_2$ in depleted oil and gas reservoirs; (3) storage of CO$_2$ in coal beds; (4) storage in salt caverns and (5) mineral storage in basalts$^1$.

**Injection into Deep Units and Reservoirs:** Conceptually for the first two methods, storage of CO$_2$ involves the injection of large volumes (millions of metric tons per year) for tens of years into a high-permeability sedimentary rock formation or a depleted oil/gas reservoir at large depth. Sequestration in the sedimentary rock formation is to be accomplished by several mechanisms including a) structural and stratigraphic trapping; b) residual CO$_2$ trapping; c) solubility trapping and d) mineral trapping (e.g., as described by Benson and Cook, 2005).

To provide some context for this process, the approximate sequestration depths for injection are on the order of 800 m to more than 3,500 m below ground surface, with temperatures of approximately 35 to 115 °C and in situ pressures in excess of 10 MPa (Nordbotten et al., 2005, Bachu, 2003)$^2$. So as not to impact the potable water supplies, the existing fluid in the injection unit (reservoir) will be non-potable, and therefore, is expected to be saline and contain a large volume of total dissolved solids (TDS). In the case of injection into a former oil/gas reservoir, the injection horizon will also contain petroleum residues.

Given the depth and temperature conditions, the injected CO$_2$ will be supercritical (sc)$^3$ (Figure 1) and anhydrous$^4$, and create a plume of approximately pure CO$_2$ near the injection point (Bryan et al., 2013). The hydrology of this horizon will displace the plume laterally, but as the density of scCO$_2$ is less than water, the fluid plume will also move upwards, especially along the increased permeability near the injection well. The center core of the plume may be entirely scCO$_2$ but as the flow migrates away from the well, the CO$_2$ plume front will mix with the existing in situ brine$^5$. As CO$_2$ is somewhat miscible in water, carbonic acid will be created, lowering the pH of the fluid. Depending on the rock mineralogy, the brine-scCO$_2$ fluid may in

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$^1$ Storage in other locations such as abandoned mines has also been suggested, but little research has been conducted in these areas (Benson and Cook, 2005). Also, deep ocean storage is not discussed here.

$^2$ Values are estimates, based on identifying typical analysis cases (i.e., warm and cold sedimentary cases) together with average thermal and pressure gradients with depth.

$^3$ CO$_2$, which is a gas at surface temperature and pressures, becomes a supercritical fluid when the CO$_2$ pressure exceeds 7.4 MPa and the temperature is greater than 31.0 °C.

$^4$ As noted by Bryan et al. (2013), transportation and pipeline operations typically require low-water-content CO$_2$.

$^5$ The CO$_2$ at the interior of the plume will also become mixed with brine with increased time.
turn react with the reservoir rock, buffering the pH and altering composition of the brine-scCO₂ fluid. This flow will continue predominantly in an upward direction until reaching a caprock, i.e., a low-permeable rock layer, almost always characterized as a shale. At this point, the flow will spread laterally along the shale-reservoir interface, but with potentially some vertical flow upward into the shale.

As the matrix of the shale is highly impermeable, the short-term flow through the rock mass will be primarily along the existing fracture networks (if the CO₂ pressure is sufficient to overcome capillary threshold pressure). With channelized flow in the caprock, the variable scCO₂-brine mixture may interact with the fracture surface depending on the mineralogy of the surface material and in turn, affect fracture flow. Further, with time, diffusion will drive chemical interactions deeper into the rock mass itself causing matrix reactions.

![CO₂ Phase Diagram](image)

Source: Modified from Bachu (2000). The critical point for CO₂ is approximately 31.05 °C and 7.38 MPa (NIST, 2015).

**Figure 1: Supercritical Region for CO₂.**
Mechanical erosion can occur along preferred fracture pathways and the flow may also interact with the clay minerals in the rock. The interaction may “dry” the caprock (replacing water \([H_2O]\) in the clay minerals) inducing contraction and cracking; or alternatively, the interaction may induce expansion and swelling pressures, and thereby reducing the fracture aperture and flow. In addition, chemical alteration of the rock may induce precipitation and dissolution, and also alter the characteristics of near-surface fracture material (e.g., reducing surface strength), which can also lead to increasing or decreasing fracture flow. Further, various trace metals in the fluid or in the rock may react, going into or out of solution. These processes will be controlled by site-specific conditions, such as the mineralogy of the units and fluid chemistry, resulting in a complex inter-relationship.

Injecting scCO\(_2\) into depleted oil and gas reservoirs is also under investigation by various organizations (Khosrokhavar, 2015). In contrast to saline reservoirs, the rock matrix of the shale plays will have reduced permeabilities but can be extensively fractured. These rock units will contain substantial organic content and potentially contain petroleum product residues as well. Sequestration will induce complex, multiphase flow conditions and physiochemical reactions. For example, injection in these units will induce CO\(_2\) to replace CH\(_4\). Further, the sorption of CO\(_2\) in the shale play units can reduce permeability of the rock (Zoback et al., 2013).

**Storage of CO\(_2\) in Coal:** The third approach to sequestration involves injection of CO\(_2\) into unmined coal units. Coal naturally contains a mixture of adsorbed gases which is approximately 80% CH\(_4\) (or more) together with minor amounts of CO\(_2\), H\(_2\)S, nitrogen (N\(_2\)), and sulfur dioxide (SO\(_2\)) (Flores, 1998). Conceptually, after injecting CO\(_2\) into the coal, CO\(_2\) replaces the absorbed CH\(_4\) present in the coal, the CO\(_2\) is trapped in the coal seam, and the displaced CH\(_4\) is extracted from the rock mass and used for energy production. This process is effective as the coal has a higher affinity to adsorb CO\(_2\) than CH\(_4\) (approximately by a factor of 2). It also has the benefit to produce energy in addition to the sequestration of CO\(_2\). This overall injection-production process is often termed CO\(_2\)-enhanced coal-bed methane (CO\(_2\)-ECBM) recovery (Masoudian, 2016).

Similar to the prior reservoir injection methods, storage of CO\(_2\) in coal involves the injection of large volumes for tens of years into a coal seam (or series of seams). The injection horizon would consist of a thin coal seam (or several seams) not economically viable for mine development. The depth for coal sequestration depends primarily on economic factors, and could range from a few hundred meters below the surface to several kilometers (Masoudian, 2016), and therefore, the injected CO\(_2\) may be a gas, liquid or a supercritical fluid.

As with prior processes, upon injection, the center core of the CO\(_2\) plume would be entirely CO\(_2\) but as flow migrates away from the well, the plume front will mix with the existing in situ fluids.
and also react with the coal itself. Mixing with existing pore fluids, carbonic acid can be created, lowering the pH of the front. As the coal matrix is relatively impermeable, initial flow through the coal horizon will be along existing discontinuities in the coal seam (i.e., fractures and cleats). However, as observed in some pilot projects and in the laboratory, coal will tend to swell with the adsorption process of CO2 (and the related desorption of CH4) (e.g., Siriwardane et al., 2009; Masoudian, 2016). This swelling significantly decreases fracture permeability with CO2 flow, and hinders the further injection of CO2 at the injection location and along preferential pathways. There is also an accompanying potential reduction in the stiffness and the strength of the coal itself with the replacement of CH4 with CO2, which in turn can also affect permeability (e.g., Wang et al., 2013; Masoudian et al., 2014; Vishal et al., 2015). This swelling and alteration can be a serious impediment to this sequestration process unless other methods are also used to stimulate flow (e.g., hydrofracture).

Storing CO2 in Salt: The fourth option of storing CO2 in salt caverns is a viable alternative, but is a more expensive solution for sequestration (Bachu and Rothenburg, 2003). Conceptually, a cavern within a salt horizon or diapir is established by using solution mining and filled with a pressurized fluid (e.g., brine). The initial fluid is then replaced over time with pressurized CO2. The storage depth is dictated by location of the salt horizon (which can be relatively shallow) and the need for an effective overburden layer above the salt to provide confinement. Given that the salt unit is insoluble in CO2 and that salt beds have a very low permeability (effectively impermeable over a period of hundred years), the major concern in sequestration in salt is the tendency of salt to deform under deviatoric stress with time, i.e., to “creep” (Bachu and Rothenburg, 2003). Therefore, after salt creep seals all openings into the cavern, the salt will continue to deform until an equilibrium pressure is reached10, potentially reducing the cavern volume. There also may be issues with temperature equilibrium. Overall, no adverse chemical reactions have been identified for this process, and the primary concern for this storage method is mechanical integrity of the cavern with time.

Storing CO2 in Basalt: Storage of CO2 in basalt (as well as other ultramafic and mafic rocks) has only recently come under serious consideration due to the results of recent field tests (Jones and Blondes, 2015). Injection of CO2 into these rocks with abundant magnesium, iron, and calcium facilitates the reaction of the fluid with the rock to form carbonates, trapping the CO2 in a solid form, often termed mineral sequestration (Aradóttir et al., 2015). These rock units, however, typically have low porosity, low permeability and low pore space continuity and may prove difficult to develop, despite their widespread occurrence11 in the world (Benson and Cook, 2005).

Initial field test have been conducted over a range of conditions, with CO2 injected in solution in water (together with H2S), as well as scCO2 injected alone. In these tests, injection depths and

10 The process depends on the compressibility and the initial pressure of the stored gas and the in situ stresses surrounding the cavity, together with the properties of the salt itself. If the initial pressure is insufficient, creep can induce fracturing in the salt, which in extreme cases, could lead to cavern failure.

11 A clear estimate of their extent is unavailable at present as described by Jones and Blondes (2015).
temperatures ranged from about 500 m at about 30 °C, to about 2,200 m at temperatures above 250°C (Aradóttir et al., 2015).

The trapping process can be complex. Briefly, upon injection, the injection fluid mixes with in situ fluids and the resulting acidic fluid reacts with the host rock, leaching cations to form carbonates along CO2 flow paths. Testing with olivine and basalts indicates that acid concentration, grain size, and mineralogy all affect dissolution rates (Qiu et al., 2012). Other experiments indicate that for reactions in high-flow zones, grain size distribution and its heterogeneities lead to the establishment of preferential flow paths, while carbonate precipitation is favored in domains of reduced flow (Andreani et al., 2009). The precipitates in the low-flow zones will tend to inhibit subsurface fracture flow, requiring minimum flow rates for the process. In summary, the process can be quite complex and is dependent on rock characteristics as well as the methods employed.

2.2 ENHANCED OIL RECOVERY AND HYDROFRACTURING

CO2 has been used in oil and petroleum production for a number of years for increasing product recovery and more-recently, in stimulating recovery in unconventional oil and gas wells using hydrofracturing.

Enhanced Oil Recovery (EOR): The petroleum industry employs various approaches to increase the amount of crude oil production after the initial pumping phase under existing conditions. During the later stages of development, various methods are employed to increase the mobility of the petroleum, and are termed, in general, as enhanced oil recovery (EOR) or tertiary recovery. One technique commonly employed during this stage is gas injection (or miscible flooding) where a miscible gas (or gas mixture) is introduced into the reservoir (at a significant distance from the production well) to drive product towards the production well (e.g., see Tzimas (2005) for additional details). A miscible fluid reduces the interfacial tension between oil and water, dissolving in the oil and reducing oil viscosity, and thereby increasing the oil recovery. CO2 is often used as it is a good solvent and is less expensive than alternatives such as liquefied petroleum gas.

The overall mobilization process in the subsurface involves complex interactions between CO2, in situ fluids and oil itself. These reactions are not fully understood, but broadly, the overall miscible flooding process can be divided into four major stages as illustrated in Figure 2. As part of the process, CO2 is often injected into sedimentary rock as a supercritical fluid and typical EOR applications are in reservoirs with medium to light gravity oils (Verma, 2015) at depth.

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12 In a similar fashion to EOR, there is a potential for the use of CO2 in enhanced gas recovery (EGR), but the technique has not yet been proven economical.

13 During the primary recovery stage, oil/gas is recovered using existing (natural) in situ pressure and conditions. Secondary recovery measures are applied when the downhole pressure can no longer drive the flow to the surface; secondary recovery procedures involve injection of fluids to increase reservoir pressure and reduce density of the fluids at the wellbore. This can involve injecting natural gas into the gas cap or at the top of reservoir and injecting water below the oil-water contact (Verma, 2015). Subsequently, more advanced, “tertiary” recovery methods are used to increase the mobility of the petroleum in the rock mass to recover additional product.
below about 800 m. The CO₂ injection process may be followed by water injection to move the CO₂ and oil towards the production well and the overall injection scheme may be repeated several times.

Some observations in using CO₂ in EOR operations are:

- EOR has been employed over large areas in a number of oil-bearing sedimentary rock types (dominantly carbonates and sandstones) without apparent adverse impact, suggesting that lithology has (in many cases) little influence on the process (Verma, 2015).

- However, in some cases, higher permeability has been observed in limestone and dolostone units as part of EOR (Bachu, 2000). This is attributed to CO₂ forming carbonic acid at depth, reducing the pH of the injected fluids, which in turn dissolve calcium in the rock and hence creates preferential pathways for flow. The reduction in pH can also lead to an increase in the concentration of calcium salts in the produced fluids, inducing observed scales in pipelines.

- Conversely, a reduction of reservoir pressure during EOR can lead to the changes in subsurface permeability due to the formation of precipitates (e.g., hydrates and asphaltenes) near the well bore, which in turn will restrict flow and reduce pressures as discussed by Tzimas et al. (2005).

- During EOR operations, some of the injected CO₂ (approximately 33% to 50% [Benson and Cook, 2005]) remains in the formation together with unswept oil and other heavier petroleum content.¹⁴

![Figure 2: Schematic of the miscible EOR process with CO₂.](image)

Source: Verma (2015, Figure 3).

¹⁴ This aspect is of importance if the same formation is used for sequestration.
Hydrofracturing: Briefly, hydrofracturing (also termed hydrofracing or fracking) is the process of inducing a fracture (or a series of fractures) underground by pressurizing a borehole in rock until the rock literally cracks. The pressure is induced by the rapid injection of a fluid into the borehole, stressing the surrounding rock until a fracture is created. Mechanically, the fracture forms parallel to the maximum principal stress existing at the borehole wall, and extends into the rock mass for some distance.

This process of fluid-based hydrofracturing as it is utilized today was developed in the late 1940’s to increase the gas or oil flow into wells located in low permeability horizons (such as low permeability sandstones and shale) (e.g., Gandossi, 2013). The use of directional drilling and the use of chemical additives together with the hydrofracture method has allowed drillers to stimulate large areas around a well in a single formation, making oil and gas recovery in these formations efficient on a large scale. This ability has allowed the large-scale production of oil and gas from rock previously assessed as too difficult and too expensive to produce by conventional means, thereby giving rise to the term “unconventional” oil and gas for this type of gas production15.

Currently, the hydrofrac process in petroleum development typically makes use of a water-based fluid (Gallegos and Varela, 2015) which can contain a number of chemical additives16 that are to facilitate downhole operations and to maintain borehole stability. During development, a weak acid may be used to clean the well before hydrofracturing. At later stages of the overall process, a fine-grained material is also added to the fracking fluid, to remain within the created fracture after the pressurization cycle and keep the fracture open, termed a proppant17.

Large quantities of water are required for hydrofrac operations. Upon completing fracturing, the fluid pressure in the well is released, and a portion (10 to 30%) of hydraulic fracturing fluid will return to the surface (flowback). This resulting fluid is now a combination of fluids, containing not only water with chemical additives, but also containing natural gases, dissolved minerals, heavy metals, and various hydrocarbons, and thus requiring the processing/treatment of flowback prior to disposal or reuse.

Given environmental considerations of flowback, alternative pressurizing fluids are being employed, including the use of CO₂ and N₂ instead of water-based systems. The advantages of using CO₂-based alternatives (liquid and scCO₂, CO₂-foam, and CO₂-N₂ mixtures) includes the reduction in the use of additives and large quantities of water for fracking together with the subsequent elimination of handling of contaminated flowback fluids.

For hydrocarbon recovery, fracking with CO₂ can be over a range of depths, and therefore CO₂ can be in a gas, liquid or supercritical phase during fracking, depending on downhole pressure

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15 Unconventional resources include production of heavy oil, coal bed methane, production in tight gas sands, development of shale oil and gas reserves, and production from gas hydrates.

16 The additives can include clay control agents (stabilizers), friction reducers, gelling agents, crosslinkers, breakers, buffers, surfactants/mutual solvents, biocides/bactericides, and other agents (see Montgomery, 2013). Typically, these additives compose less than 0.5% of the fracture fluid (GWPC-ALL, 2009).

17 Most often, the proppant is a natural uniform fine sand, a resin-coated sand or a uniform ceramic material, ranging in particle size of about 106 µm to 2.36 mm (Horiba, 2016).
and temperature. The flow into the formation along the generated fracture can be similar to sequestration but can be more turbulent, readily mixing the CO\textsubscript{2} and in situ fluids. It is important to note that CO\textsubscript{2} dissolves in water/brine downhole, creating carbonic acid, which can control clay swelling and iron and aluminum hydroxide precipitation, as well as reacting with carbonate rocks (Gandossi, 2013). There can also be desorption of CH\textsubscript{4}, the trapping of CO\textsubscript{2} in organics contained in the shale (kerogen), and the generation of thermal stresses which can induce cracking (Middleton et al., 2014).

Hydrofracturing is also used in the development of geothermal systems, discussed in the next section.

2.3 GEOTHERMAL SYSTEMS

A relatively new concept is the use of CO\textsubscript{2} in geothermal applications (Brown, 2000). In this application, scCO\textsubscript{2} is circulated into hot rock underground and then returned to the surface to bring heat to generate electricity. The heat of the scCO\textsubscript{2} is transferred by conduction to a secondary fluid turbine or the scCO\textsubscript{2} is directly used to generate power through a supercritical CO\textsubscript{2} turbine before being sent back to the reservoir. The injection formation can be in fractured units of basement rock\textsuperscript{18} or sedimentary formations.

The advantages in using scCO\textsubscript{2} rather than water include (Brown, 2000):

1. Density difference between the cold scCO\textsubscript{2} at the surface and hot scCO\textsubscript{2} provides a large buoyant drive reducing the required circulating pumping power

2. Reduced ability of scCO\textsubscript{2} to dissolve and transport mineral species (in deep basement rock) eliminates scaling in surface piping, and other equipment

3. Reduced problems associated with silica dissolution in developing reservoirs (in deep basement rock) at temperatures in excess of 374 °C (the critical temperature for water), potentially providing increased thermodynamic efficiency

Several variants of the basic CO\textsubscript{2}-injection concept have been proposed. For example (Ahmed and Javed, 2014):

1. The concept by Brown (2000) involves an extension of the geothermal study of the deep injection in deep hot rocks, where scCO\textsubscript{2} would be circulated (instead of brine) at depths on the order of 4 km. The target reservoir for circulation would be in fractured basement rock at temperatures of approximately 260 °C and pressures of 30 MPa. The system would be created by first hydrofracing the target rock at depth to establish a closed loop in the subsurface to extract heat. It is expected that dissolved water will be present in the production stream.

2. An alternative concept, the CO\textsubscript{2}-plume geothermal (CPG) (Randolph and Saar, 2011), would circulate scCO\textsubscript{2} at shallow depth, on the order of 1 km. In this concept, the target reservoir is sedimentary in origin with reduced fluid temperatures (roughly 100 °C) and

\textsuperscript{18} Basement rocks are defined as rock units below the sedimentary platform or basin, and are igneous or metamorphic in origin.
pressures of about 25 MPa. A large plume would be created below a thick, low permeability caprock, containing/trapping the injected CO$_2$ which would be pumped downstream to obtain heated fluid (without the use of hydrofracturing) to create the loop between the injection and production wells. The system is envisioned to be used with large CO$_2$ sources for injection, and involves substantial CO$_2$ loss in the subsurface. Again, dissolved water will be present in the production stream.

3. Other approaches involve the use of hybrid systems combining CO$_2$ and brine injection to use both fluids for energy production formations (Buscheck et al., 2012) or CO$_2$ injection to assist brine-based systems (Salimi and Wolf, 2012). Further, a recent hybrid concept combines geothermal-like operations with CO$_2$ sequestration to store energy (Buscheck, 2015). The depths and pressures for these methods appear similar to sequestration injection in sedimentary rock as discussed earlier, and involve the deliberate, large loss of injected CO$_2$ in the subsurface.

A number of technical issues have been identified in developing geothermal energy (e.g., MIT, 2006; NSF-SEES, 2011); the issues more directly related to the use of CO$_2$ include:

- Rock-fluid interactions can significantly affect the target horizon permeability. In sedimentary units, short-term and long-term reactions of CO$_2$-brine at elevated temperatures and pressures can alter the reservoir fractures and thereby reduce or increase the permeability of the circulation loop. Little data exist on especially long-term reaction/alteration processes and rates to predict where and when these effects will occur (MIT, 2006).

- Effects of thermal and stress changes on multi-phase fracture flow with flow from cold to hot regions during the cycle are expected to be complex and a clear theoretical basis is not established.

- The effects of higher pressure may induce adverse conditions. The need for high flow rates during geothermal operations (and the attendant higher downhole pressures) will increase fracture permeability by increasing aperture height; fractures may also shear and perhaps extend under these conditions, all of which can grow the flow area in the reservoir.

- As with brine, CO$_2$ at higher pressures during the various stages of these processes can effect nearby fault stability and potentially induce local seismic events. Induced seismicity at a site can occur depending on the rate and amount of fluid injected, the orientation of the stress field relative to the pore-pressure increase, the location and extensiveness of the local fault system, and the magnitude of the deviatoric stress field in the subsurface (Majer et al., 2007).

- Other factors involved in the geothermal development have also been hypothesized to be factors that could induce fault instability, such as volume withdrawal, temperature decrease due to colder injected fluids and chemical alteration of the fracture surfaces (Majer et al., 2007).

- Given the fractured nature of the reservoir rock and in situ conditions, creating new fractures (with CO$_2$ or brine) may prove problematic, as borehole pressurization may instead open and shear existing, favorably-oriented fractures along the borehole.
• Heterogeneity of the target rock formation significantly influences both heat extraction and CO₂ storage.

2.4 SUMMARY OF CONCERNS WITH PROCESSES

In summary, CO₂ is being utilized in the subsurface for differing reasons. Some aspects of interest in the range of current application are:

• CO₂ is the key component in a number of subsurface processes. It is actively being used in petroleum-related operations, and could be beneficial in geothermal energy. In addition, sequestration of CO₂ is under extensive investigation to address climate concerns; this application involves scCO₂.

• Under the wide range of in situ conditions for these processes, the phase of CO₂ will change depending on pressure/temperature conditions. Therefore, changes in CO₂ phase need to be considered in evaluating the in situ CO₂ response.

• CO₂ itself is not the only fluid component in these processes, and the potential for fluid mixing (e.g., CO₂-brine mixtures) and multiphase flow must be considered in assessing in situ response.

• As observed, the replacement of CH₄ by CO₂ will induce swelling with coal and effect large-scale permeability, but the reaction of CO₂ with other finely-grained sedimentary units is not demonstrated with the stated processes.

• The physiochemical interactions of the rock unit (and organics), with CO₂ and the in situ fluids can be complex and can have a direct bearing on the engineering application in the field. This is especially important in sedimentary rock units.¹⁹ The mineralogy of the rock (and its variability) will therefore be very important to process planning.

• CO₂ injection can increase the effective permeability of units containing substantial carbonate content due to acidic-based dissolution, as observed in EOR operations. This chemical reaction can also have an effect in ultramafic and mafic rock units, depending on flow rate. However, apparently CO₂ flow has little apparent effect (essentially, the flow is lithologically-independent) when CO₂ is employed in EOR with other more-permeable sedimentary units.

• Changes in in situ pressures from the processes can potentially induce adverse response (seismicity).²⁰

• To summarize, the response of fractures and the overall rock mass to CO₂ flow is dynamic, path-dependent and time-dependent. Interactions can potentially induce shrinkage or swelling of the rock as well as dissolution, erosion or precipitation along the fracture, all of which affects the transmissivity of the rock mass. These aspects are

¹⁹ Note, this also implies the fluids used in laboratory testing can also affect response, and the use of pure distilled water may provide misleading results as used in many permeability tests.

²⁰ For sequestration, induced seismic events can be considered unlikely if sited and injections are conducted with care (Vilarrasa and Carrera, 2015)
interactive and alter the conditions along the flow path at different positions. The interactions can be time-dependent, as the diffusion of alteration into the rock matrix will take substantial periods of time. Given an interconnected fracture network and channelized flow along the fractures, the flow path through the fractured rock will also change with time.21

- Not discussed in the foregoing process summaries, but still of major significance, is the impact of the fabric of the rock mass on in situ applications. The rock fabric, especially the (large-scale) macrofabric, is often not well defined in most applications, but it can have major impacts on flow and in the utilization and ultimate success of the specific process. As an example, hydrofracturing in fractured rock can be problematic where the discontinuities have less strength than the rock matrix, preventing the formation of new fractures.

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21 For example, the restriction of flow along the section of a fracture can divert flow to other parts of the same fracture or along entirely different fractures and paths.
3. IDENTIFICATION OF ROCK UNITS

3.1 GENERAL

In examining the response of very-fine-grained clastic sedimentary rock\textsuperscript{22}, it becomes necessary to clearly identify the rock type under study. Unfortunately, the term, “shale” and methods of identifying this rock type are ambiguous in the literature. Therefore, it becomes necessary to first discuss classification methods to be able to identify a clear basis for the subsequent review.

As noted by Wilkins (2011):

\begin{quote}
Ideally, any classification should be comprehensive, scientifically sound, unambiguous, practically-oriented, easy to use, and avoids unclear, undefined terminology. The advantages of such a classification are the standardization in the reporting of results and their effective communication between users.
\end{quote}

The following sections discuss various approaches to define “shale,” and very-fine-grained rock in general.

3.2 WHAT IS A SHALE?

The term “shale” is readily understood by various technical professionals dealing with the subsurface conditions. Unfortunately, how the word shale is defined can differ with the technical specialty. Further, there are a number of related terms such as argillite, claystone, clayrock, lutite, marl, mudrock, mudstone, physilite, and siltstone in the technical literature, all of which further confuse the issue of defining a shale.

As discussed by Tourtelot (1960), the word shale arises from the mineral industry in England, first recorded in the 1700s and has been applied to a variety of fine-grained rocks. For example, slate was also identified with the term shale as late as the 1920s. To summarize, historically, “shale” has three major definitions (Wilkins, 2011):

1. Term for describing a very-fine-grained, laminated (fissile) clayey rock
2. Formation name, e.g., as the “Pierre Shale”
3. Term incorporating all very-fine-grained rocks (whether they are laminated or not)

The first, more-specific, definition of shale as a type of fissile clayey rock is generally used as part of a lithologic system which describes the general array fine-grained sedimentary rock types in geology (together with terms such as mudstone, siltstone, etc.). Regrettably, there is no accepted standard geologic definition of shale, despite various efforts. In addition, due to current use of the more general definition of shale by the general public, some geologists have proposed that the term shale should not be used at all by geologists to describe fine-grained rock types (e.g., Lundegard and Samuels, 1980; Macquaker and Adams, 2003), substituting the generic

\textsuperscript{22} For this report, fine-grained sedimentary rock is defined as having a predominant particle size < 2 mm (sand size), with very-fine-grained rock having a predominant particle size < 0.063 mm (silt-clay size).
term, “mudstone.” This position is apparently becoming accepted in the geologic community (Boggs, 2009).

The third, all-encompassing, definition is more prevalent in the engineering disciplines, where it is employed with various implicit characteristics or restrictions. However, without some clarifications of these characteristics, the term is too general and ill-suited to more scientific study. Many times in engineering literature, shale has become essentially a catchall term and of little value in understanding the characteristics of the material.

### 3.3 LITHOLOGIC CLASSIFICATION OF FINE GRAINED SEDIMENTARY ROCK

In the last 100 years, a variety of lithological classification systems have been proposed for fine-grained sedimentary rock. As noted by various authors (e.g., Weaver, 1989; Boggs, 2009; Lazar et al., 2015), these systems have utilized a variety of nomenclature including lutite, siltstone, mudstone, mudrock, claystone, clayshale, shale, and marl to describe various groupings. These lithological classification systems have focused on the visual characteristics of the rock (i.e., particle size, texture, hardness and color) to describe rock categories, and often with major distinctions based on the general grouping of particle size.

The particle size of classification systems for rock employ the same grain size terms developed for the classification of soils (unconsolidated sediments) and hence the terms, sand, silt and clay are used to describing the particle size variation. Limiting the discussion to (fine-grained) rock units with a predominant particle size of less than about 2 mm (considered to be the upper size boundary of a sand), particle-sized classification systems commonly divide the rock matrix into three groups: 1) sand-sized, 2) silt-sized, and 3) clay-sized particles; the percentage of each group are typically based on weight after deaggregation of the sample. To describe the percentages in a graphical manner for three all-inclusive variables, a ternary diagram is used (e.g., as shown in Figures 3 and 4).

The actual particle size bounds can vary with the particular rock classification system and do not always correlate with common soil classification terms. For example, the boundary between silt and sand sizes is taken as 0.075 mm in the Unified Soil Classification System (USCS) for soils (see ASTM D2487), but is defined as 0.0625 mm in the Udden-Wentworth system (Wentworth, 1922).23

It is observed that most sedimentologists employ the Udden-Wentworth size system (Wentworth, 1922), or a variant, the Krumbein “phi scale” (Krumbein and Aberdeen, 1937) for grain size definitions, and therefore, the latter system will be adopted in this report (Table 1). The reader should note that the clay size term does not directly correlate with the actual mineral content. Specifically, all clay-sized particles in a shale are not necessarily clay minerals, but rather can be composed of a number of non-clay clasts as well as clay minerals. Further, the size of clay particles can range in size above 3.9 μm size limit and can form structures as large as 150 μm or

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23 The two classifications systems use different sieve sizes to define particle size. For example, to define fines (i.e., particles less than sand-size); the USCS uses a #200 sieve, while the Udden-Wentworth system uses a #230 sieve.
silt-sized (Weaver, 1989). Therefore, it is important to distinguish between clay-size component of the matrix and the amount of clay minerals when discussing classifications.

Table 1: Particle Size Scales

<table>
<thead>
<tr>
<th>Term</th>
<th>Udden-Wentworth Scale</th>
<th>Krumbein Phi System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>1/16 to 2 mm</td>
<td>4 to -1&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Very coarse sand</td>
<td>1 to 2 mm</td>
<td>0 to -1</td>
</tr>
<tr>
<td>Coarse sand</td>
<td>1/2 to 1 mm (0.5 to 1.0 mm)</td>
<td>1 to 0</td>
</tr>
<tr>
<td>Medium sand</td>
<td>1/4 to 1/2 mm (0.25 to 0.5 mm)</td>
<td>2 to 1</td>
</tr>
<tr>
<td>Fine sand</td>
<td>1/8 to 1/4 mm (0.125 to 0.25 mm)</td>
<td>3 to 2</td>
</tr>
<tr>
<td>Very fine sand</td>
<td>1/16 mm to 1/8 mm (62.5 µm to 125 µm)</td>
<td>4 to 3</td>
</tr>
<tr>
<td>Silt</td>
<td>1/256 to 1/16 mm (3.9 to 62.5 µm)</td>
<td>8 to 4</td>
</tr>
<tr>
<td>Clay</td>
<td>Less than 1/256 (Less than 3.9 µm)</td>
<td>&gt; 8</td>
</tr>
</tbody>
</table>

Note:

<sup>a</sup> The Krumbein Phi System defines the diameter in terms of a dimensionless value, phi, expressed as

\[ D = D_o \times 2^{-\phi} \]

where \( D \) is the particle size, \( \phi \) is an integer, \( D_o \) is the reference dimension of 1 mm. The particle size decreases with increasing phi value.

<sup>b</sup> The silt size is often rounded to 63 µm.

<sup>c</sup> Size values are from Wentworth (1922) and Krumbein and Aberdeen (1937)

<sup>d</sup> Note that the equation incorporates a negative power, so the \( \phi \)-scale numbers for a range are shown from large to small to describe the resulting size range from small to large.

In defining shale, a characteristic for classification of a shale is the tendency of the matrix to separate along thin laminations in the rock and to form thin sheets. In more detail, due to the depositional origin of fine-grained sediments, the rock fabric tends to exhibit transverse anisotropy and can contain various discontinuities along the plane of deposition. Bedding planes, changes in particle gradation (e.g., sands lens), and clay mineral orientation can produce laminations in the texture of very-fine-grained sedimentary units. In particular, the tendency to separate along planes/laminations at spacings of less than 1.0 mm is defined as fissility<sup>24</sup>. The fissility of the rock matrix can be suggestive of increased clay mineral content as fissility tends to

<sup>24</sup> The texture is termed papery at spacings less than 0.5 mm, and other terms are used to describe larger spacings (Potter et al., 1980).
decrease with increasing calcareous and siliceous material content (Weaver, 1989). However, some authors discount fissility as a product of weathering and as a function of water content and temperature, and should not be used as a basis for shale classification (e.g., Lundegard and Samuels, 1980; Wilkins, 2011; Lazar et al., 2015).

Rock units are also divided by the apparent hardness or friability (induration) of the unit, where hardness is based on the ability of the rock matrix to be reduced to smaller pieces with little effort in handling. In this regard, rock units are divided into two groups: 1) indurated rock, which is difficult to break with a geologic hammer, and 2) non-indurated rocks, which readily break apart in your hand. The non-indurated rock would include sediment that lacks cementation (as from carbonate content). Unfortunately, the distinction between non-indurated (soft) rock and hard, dense soils remains ambiguous with this terminology.25

Finally, the classification of fine-grained sedimentary rock can employ color. The color of the rock matrix can be affected (to a degree) by the organic content of material. Generally, the colors red and purple are associated with low organic content in contrast to grey and black, which typically indicate high organic content (e.g., black shale) (Potter et al., 1980).

As mentioned, a number of lithological classifications systems have employed these parameters to classify fine-grained sedimentary rock (e.g., Boggs, 2009). However, only a limited number are examined in this report, sufficient only to demonstrate the range of approaches and provide a basis for the evaluation of limitations.

An early classification system is proposed by Folk (1954) as shown in Figure 3. The system divides particle size of the fine-grained sedimentary rock into ten types based on three groups or ranges of particle size (sand-silt-clay). Division of the content of the fines (i.e., less than 0.063 mm) is structured primarily based on a ratio of silt-size to clay-size content. The system also employs fissility as a basis for the nomenclature. The system identifies two sets of category names, using the suffix “-shale” (as in “clayshale”) for units that are fissile, and using the suffix, “-stone” for more-massive units (e.g., claystone). This results in 16 separate categories for fine-grained rock. A similar, more-simplified system is proposed by Wilkins (2011).26

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25 Some authors have attempted to address this concern in field classification; for example the distinction of soil versus rock is indicated by the ability to mold the sample between the fingers when wet, as suggested by Merriman et al. (2003)

26 Wilkins (2011) divides very-fine-grained rock into only three categories: 1) claystone; 2) mudstone, and 3) siltstone, based on ratios similar to Folk (1954), but without the presence of fissility as a criterion for classification.
Figure 3: Classification of sedimentary units based on grain size and silt-clay ratio by Folk (1954).
Source: Modified from Picard (1971); grain size limits based on Krumbein phi scale for grain size (Krumbein and Aberdeen, 1937).

Figure 4: Classification of sedimentary units based on grain size by Picard (1971).
Another classification system for fine-grained sedimentary rock was developed by Picard (1971) and is shown in Figure 4. The categories are grouped into four more-general groups: 1) claystone, 2) siltstone, 3) mudstone, and 4) sandstone (Figure 4a). Each of these general groups are further divided into three sub categories, using an adjective to define the sub category (e.g., clayey sandstone) (Figure 4b) for a total of 12 categories. A distinction on fissility is described separately, and the term shale is not used in this system.

Other systems have focused only on the very-fine-grained component of sedimentary rock (i.e., the portion of the material where the particle size is less than 0.062 mm) and on rock that is indurated. For example, two similar systems are shown in Figure 5 and Figure 6 by Potter et al. (1980) and Lundegard and Samuels (1980)27. Both systems classify the units based on fabric (lamination) and the clay-size content, and use the distinction of “-stone” for non-laminated rock and “-shale” for laminated rock. Nonindurated sediment is classified using soil terminology such as silt and mud.

Up to this point, the classification systems discussed are based on particle size as function of weight, requiring de-aggregation of the sample. In contrast, the system proposed by Lewan (1978), uses microscopy to defined particle size categories (shown in Figure 7), and uses a weight-based distinction only on the silicate fraction. The silicate fraction is defined as the fraction of the tektosilicates, phyllosilicates, chalcedony, and glass to the sum of silicate and nonsilicate content28. Microscopic material is defined as particle size finer than 5 μm. The need for particle size measurement is eliminated and replaced by matrix mineralogy analysis. Note that this system divides the rock into only four categories, but using less typical terms such as marlstone, and micstone29.

A more recent classification system based on particle size was proposed by Macquaker and Adams (2003). On one level, the system simplifies the category names, employing the single term, “mudstone”, for all very-fine-grained rock (i.e. units with more than 50% content with a particle size less than 63 μm). However, complexity remains, as 14 sub-categories are defined by two sets of content modifiers, using terms such as bearing or rich (see Figure 8).

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27 Both systems are evolved from Blatt et al. (1972).

28 The denominator is the sum of the silicate content as well as the contribution of nonsilicates including carbonates, phosphates, chlorides, sulfates, iron oxides, manganese oxides, and aluminum oxides. The denominator does not include the content due to sulfides (e.g., pyrites) or organic matter.

29 Abbreviated form of micritic limestone (Potter et al., 1980).
| SHALE: Fine-Grained Sedimentary Rock (More than 50% Grains by Weight Are Less Than 0.062 mm in Diameter) | Percentage Clay-Size |
|---|---|---|
| Indurated Fabric | Bedded (Separations Spaced Greater Than 10 mm) | Bedded Siltstone | Mudstone | Claystone |
| | Laminæ (Separations Spaced Less Than 10 mm) | Laminated Siltstone | Mudshale | Clayshale |

Source: Modified from Potter et al. (1980).

Figure 5: Lithologic classification of sedimentary rock by weight from Potter et al. (1980).

| MUDROCK - Fine-Grained Sedimentary Rock (More than 50% of Grains by Weight Are Less Than 0.062 mm in Diameter) | Percentage Clay-Size |
|---|---|---|---|
| Indurated Fabric | Non-Laminated | Siltstone | Mudstone | Claystone |
| | Laminated - Separations Spaced Less Than 10 mm | Mudshale | Clayshale |

Source: Modified from Lundegard and Samuels (1980).

Figure 6: Lithologic classification of shales by weight by Lundegard and Samuels (1980).

| SEDIMENTARY ROCK: Fine-Grained Sedimentary Rock (More than 45% Grains by Volume are Less than 62 μm in Diameter) | Silicate Fraction by Weight |
|---|---|---|---|
| Volume % Microscopic Shale (More than 65% of Grains by Volume Are Smaller Than 5 μm) | Micstone | 0% to 25% | Marlstone | 26% to 74% | Claystone | 75% to 100% |
| | Mudstone (Less than 65% of Grains by Volume Are Smaller Than 5 μm) | Mudstone |

Source: Modified from Lewan (1978).

Figure 7: Classification of very fine grained sediments by volume by Lewan (1978).

Figure 8: Classification of mudstones by grain size by Macquaker and Adams (2003).
Table 2: Classification System Based on Particle Size and Clay Content Using the Term *Physil* by Weaver (1989)

<table>
<thead>
<tr>
<th>Texture</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unindurated</td>
</tr>
<tr>
<td></td>
<td>&gt; 50% Physils</td>
</tr>
<tr>
<td>≥ 50% Silt Sized Particles</td>
<td>physil silt</td>
</tr>
<tr>
<td>[1/256 to 1/16 mm]</td>
<td></td>
</tr>
<tr>
<td>&gt; 50% Clay Sized Particles</td>
<td>physil clay</td>
</tr>
<tr>
<td>[&lt;1/256 mm]</td>
<td></td>
</tr>
</tbody>
</table>


Note: “Physil” is an abbreviated form of phyllosilicate.

Most classification systems use lithologic names commonly found in the technical literature. However, one lithological classification system has taken a different tack, eliminating the term shale altogether, and introducing the term, “physil”, as an abbreviated form of “phyllosilicate.”

The term physil is used to indicate the clay mineral content (Weaver, 1989). The intent is to clearly separate the particle size terminology from the clay mineral content. The classification of very-fine-grained clastic sedimentary rock uses two general groups for indurated rock defined based on particle size: 1) siltstone and 2) claystone (Table 2). Two adjectives are introduced based on clay mineral content: the rock is termed “physil” if it contains more than 50% phyllosciates; and “physilitic” if it contains less than 50%. For example, units rich in clay minerals then would be labeled as either physil claystone or physil siltstone.

In summary, various particle-based lithologic systems have been proposed. These systems were developed primarily for field classification and use a variety of terms. The systems often differ in basic structure, based on underlying assumptions. Of major importance, none of these systems have been widely accepted in the literature. Also, the relationship of the stated categories to material behavior was not demonstrated by the source references.

### 3.4 MINERALOGY OF SHALE AND FINE-GRAINED ROCK

Mineral constituents can also be used to classify fine-grained sedimentary rocks, though mineral results are infrequently reported in the literature when discussing shales. For fine-grained sedimentary rocks, the material constituents can be divided into broad categories which can allow classification. A common approach is to divide the material components into three, all-

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30 Clay minerals are typically defined as phyllosciates, as discussed later in this report.
encompassing categories: (1) carbonates (including calcite and dolomite); (2) clay mineral content, and (3) quartz-feldspar and other components. This allows for use of a ternary diagram (e.g., Figure 9), similar to particle size classifications.

The definition of these groups is somewhat arbitrary, but the total minerals in the resulting groups must sum to 100%. The last category, “quartz feldspar and other components”, is generally a catchall for the low-percentage mineral content and metal oxides that may be present in the matrix. The definition of the clay minerals category is expanded in this context to include organic content included in the rock matrix.

Various authors have attempted to define the average mineral content of shales. As discussed by Yaalon (1981), prior to 1950, the clay mineral content of typical shales was assessed to be low, less than 50%, and approximately equal to 35%. However, with more updated testing, this concept has changed. For a range of “typical” shales from Russia and America reported by various authors, the average mineral content was assessed as 59% clay minerals, 20% quartz and chert, 8% felspars, 7% carbonates, 3% iron oxide minerals, 1% organic matter and 2% other minerals (Yaalon, 1981). The author also identified a range of results, estimating that the shales studied contain 47% to 69% clay minerals and 1% to 4% organics. The range of carbonates in these rocks was low, ranging from 4% to 13%.

Plotting the typical shale average and range of results places these units in the upper left corner of a ternary diagram, with the clay mineral content at the top of the diagram (see Figure 9). The average value for shale from Yaalon correlates well with estimates by other authors (e.g., Shaw and Weaver, 1965; Taylor and Smith, 1986). Mineral constitute diagrams shown by Potter et al. (1980) indicate that the “shales” category contain 50% to 100% clay minerals. In contrast, values provided by Boggs (2009) indicate a wider range of 17% to 57% clay mineral content for shales, based on the work of O’Brien and Slatt (1990)\(^{31}\). However, the carbonate content (i.e., primarily calcite, dolomite and siderite) ranged from roughly 4% to 17%, similar to Yaalon (1981).

In addition to such efforts to identify the mineralogy of average shales, there have also been various efforts in recent years to classify sedimentary rock using these three general mineral categories (e.g., Füchtbauer, 1959; Bhatia, 1985; Allix, 2010; Boak et al., 2012). Some of these systems have fewer than 10 subcategories, but as for lithologic classifications, each of these systems is distinctive, and no consensus exists on identifying shale.

With recent unconventional gas instrument development, some of these mineralogical classification systems incorporate downhole measurements systems to classify rock units. For example, the iCore system by Kumar and Kear (2003) divides the fine-grained sediments into three general categories based on mineral content: (1) shales and marls, (2) carbonates, and (3) sandstone (Figure 10), with a total of 12 subcategories. The classification system makes use of a borehole spectroscopy tool used in borehole surveys. The tool generates a continuous output of mineralogical data, which in turn are used to categorize rock units.

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\(^{31}\) There is also data on Utica Shale and the Wilcox Group indicating a 19% carbonate content (O’Brien and Slatt, 1990).
Similarly, another system, the sCore system, has also been proposed for very-fine-grained sedimentary rock by Gamero-Diaz et al. (2012). The system is based on a combination of core- and log-based mineralogical relationships, and classifies all very-fine-grained sedimentary rock as mudstone, with adjectives to further refine the classification into four main groups: (1) argillaceous mudstones, (2) siliceous mudstones, (3) carbonate mudstones, and (4) mixed mudstones (Figure 11). Each group is further subdivided into four subcategories for a total of 16 subcategories based on relative mineral content, defined using a second adjective (rich-, mixed – or -dominated).

As a further refinement, recent classifications have combined the lithological classification of fine-grained rock with mineralogical descriptors to develop a more comprehensive material description. Lazar et al. (2015) proposed an integrated nomenclature scheme using a root term mudstone for very-fine-grained rock (< 62.5 µm), modified by description of bedding, composition, and grain origin. The texture is further described as coarse, medium, or fine, depending on the predominant particle size. Bedding descriptors are based on Campbell’s (1967) genetic approach, and the mineralogical composition is described as siliceous, calcareous, or argillaceous (for mineral content greater than 50%) or defined by various hybrid terms using these terms in the central region of the ternary diagram.

![Figure 9: Typical shales classified by mineral content.](image-url)
Figure 10: iCore classification of units using mineral content by Kumar and Kear (2003).
Figure 11: sCore classification of units using mineral content by Gamero-Diaz et al. (2012).

Source: Modified from Gamero-Diaz et al. (2012).
3.5 CIVIL ENGINEERING CLASSIFICATION OF SHALE

The classification of shale for civil engineering purposes mirrors the underlying emphasis of the engineering field, specifically, the strength and durability of materials as part of structural design. Rock units are classified as shale defined primarily by the factors of durability, strength, plasticity, and anisotropy.

Civil engineering definitions of fine-grained sedimentary rock and shales in particular have been proposed by a number of authors. Implicit in these definitions is often the understanding that the material has significant clay content:

1. Mead (1936) divides all fine-grained rock (shale) into two categories: (1) compaction shales with little or no intergranular cementation; and (2) cementation shales which have experienced a cementation or “setting” process in addition to the compaction process. The compaction shales will disaggregate when acted upon water subsequent to drying.

2. Underwood (1967) based the definition of shale on lithologic distinction of “insoluble” very-fine-grained rock units (siltstone and claystone) with the distinction that shales exhibit fissility, citing the work by Philbrick (1950) (Figure 12). The shale category is further divided to (1) soil-like and (2) rock-like, based on the strength of the rock matrix.

3. A strength/compressibility based system was proposed by Deere (1968) for all rock types. For shales, the classification separates shales into “hard” and “soft” shales, divided at a uniaxial strength of about 27 MPa (Figure 13). Most shales are classified as having an average or low modulus ratio, and the shale groups exhibits a wide range of strength values (from 1 to about 200 MPa). A lower value of strength is not explicitly defined in the source.

4. Deo (1972) divides shales into four categories: (1) rock like shale; (2) Intermediate-1 shale; (3) Intermediate-2 shale; and (4) soil-like shale, based on slake-durability testing of dry and soaked samples, together with a soundness test, modified from ASTM C 88-6333. The purpose of the classification was for embankment performance.

5. Morgenstern and Eigenbrod (1974) divides argillaceous material into two categories: (1) clay and (2) mudstone (shale if fissile) based on uniaxial strength of 1.7 MPa (250 psi), and the material can be further described in terms of slaking characteristics.

6. Franklin (1981) evaluated shale for engineering purposes using a chart-based shale rating system, with values ranging from 0 to 9 (from bad to good). The chart is illustrated in Source: Figure modified from Franklin (1981). Equations were developed from source figure.

Note: Rs = Shale Rating System Value; PI = plasticity Index (%); SD = slake durability index (%); PS = point load strength (MPa).

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32 Insoluble rock is defined as where cavernous conditions do not occur naturally.

33 The ASTM procedure is used to determine the resistance of aggregates to disintegration by sodium sulfate or magnesium sulfate. The modification uses a reduced saturation of the chemical solution.
7. Figure 14. The system uses slake durability to divide the categories at the 80% slake durability line, and then uses the plasticity index (PI) (for low durability values) or the point load strength (for high durability values) to determine the rating value. The rating value was correlated by the author to excavating methods, foundation properties, embankment construction, and slope stability.

8. A more extensive program of slake testing with different durations to classify shales was described by Hopkins and Deen (1983). The authors concluded that the test was applicable to classifying shale and that a fairly good correlation was obtained between the slake-durability decay index and the natural water content of a shale. However, the slake testing showed no meaningful correlation with oedometer swell test results.

9. Based on a review of engineering classification systems, Ezzat (2005) concluded that three conditional values are required prior to dividing the argillaceous material into either soil or rock: (1) undrained shear strength, (2) the degree of strength loss after softening, and (3) the degree of change in water content after softening. However, the author does not identify a preferred classification system.

10. A more ambitious classification system is defined by Grainger (1984), where fine-grained sediments are defined as (a) soil, (b) non-durable mudrock, or (c) durable mudrock, based on uniaxial strength and slake-durability testing (Figure 15). Categories of non-durable and durable rock are further delineated based on quartz content and an anisotropy index (either with a flakiness index or the strength ratio of the uniaxial strength perpendicular/parallel to bedding). The division results in 11 categories of very-fine-grained sediments.

Often, the engineering classification of shales and material response (especially for swell) are focused on a specific engineering application. In addition, the categories divided based on the index properties such as Atterberg Limit determinations (Atterberg, 1911), dry density, porosity, as well as based on more sophisticated tests such slake-durability and compressive strength, and many times designated with a numerical index (e.g., as for swell). The distinction is combined with lithological descriptions (e.g., Shale Unit B) are significantly site-dependent and purpose-driven, and cannot be readily transferred from site to site (Underwood, 1967).

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34 Franklin (1981) provides a chart to determine values; for ease of use, the chart has been reduced here to equational form, shown below the figure.
Sedimentary Rock

Insoluble*
- Coal
- Sandstone / Conglomerate
- Siltstone
- Claystone

Soluble
- Limestone
- Dolomite
- Evaporites

Shale

Soil-Like Shale
  Compacted: Lacks Granular Cement

Rock-Like Shale
  Cemented or Recrystallized

Argillite
Slate
Schist

+ Fissility
+ Metamorphism

* Insoluble Rocks are Defined as Composed of Insoluble Minerals in which Naturally Cavernous Conditions do not Occur

Source: Modified from Underwood (1967), based on discussions by Philbrick (1950).

Figure 12: Engineering classification of shale by Underwood (1967).
Figure 13: Engineering classification of shales based on strength, and compressibility from Deere (1968).
Chart for Franklin’s Shale Rating System ($R_s = 0$ to $9$):

![Shale Rating Chart](image)

**Equational Representation:**

<table>
<thead>
<tr>
<th>$R_s$</th>
<th>Equation</th>
<th>Condition</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$R_s = 0$</td>
<td>$SD &lt; 80$ and $PI &gt; 50%$</td>
<td>$EQ. \ 1a$</td>
</tr>
<tr>
<td></td>
<td>$R_s = 0.05 \times \left{ \text{ATAN} \left[ 2.08 \times \frac{(50 - PI)}{(80 - SD)} \right] \right}$</td>
<td>$SD &lt; 80%$ and $PI \leq 50%$</td>
<td>$EQ. \ 1b$</td>
</tr>
<tr>
<td></td>
<td>$R_s = 4.5 + 0.05 \times \left{ \text{ATAN} \left[ 0.0655 \times \frac{(SD - 80)}{(2 - (\log(PS) + 1))} \right] \right}$</td>
<td>$SD \geq 80%$ and $0.1 &lt; PS &lt; 10$ MPa</td>
<td>$EQ. \ 1c$</td>
</tr>
<tr>
<td>9</td>
<td>$R_s = 9$</td>
<td>$SD \geq 80%$ and $PS \geq 10$ MPa</td>
<td>$EQ. \ 1d$</td>
</tr>
</tbody>
</table>

Source: Figure modified from Franklin (1981). Equations were developed from source figure.

Note: $Rs =$ Shale Rating System Value; $PI =$ plasticity Index (%); $SD =$ slake durability index (%); $PS =$ point load strength (MPa).

Figure 14: Rating system using durability, strength and plasticity index for shale from Franklin (1981).
Figure 15: Engineering classification of Mudrocks based on strength, durability, content, and anisotropy by Grainger (1984).
Also, implicit in the use of the term shale in many civil engineering applications is that rock material has a significant clay content and that shale can be addressed in the similar manner as clay for design purposes. As the bound between “hard clays” and “soft rock” is not well defined, discussions on engineering topics such as swell are essentially merged for clay and shale, ignoring the underlying differences in material fabric due to the lithification process.

To summarize, the civil engineering definition of shale is more numerically-based, uses a lithologic classification system in part, but the rock material is defined by index and other test results and the material is often assumed to be significantly argillaceous in content.

3.6 PETROLEUM ENGINEERING – OIL SHALE, OIL AND GAS BEARING SHALE

Fine grained sedimentary rock units that are the focus of petroleum and natural gas production are typically described as oil-bearing shale, or gas-bearing shales, and under specific conditions, oil-shale. Areas of petroleum and gas development are often described as “shale plays” with several major shale plays identified spanning the continental United States (e.g., EIA, 2011). In classifying these producing units as shale, the petroleum engineering focuses on the ability of the fine-grained sedimentary unit to produce oil or gas (such as oil-bearing or gas-bearing shale) or on the organic content of the unit that can be used in petroleum production (oil shale). The term shale is, therefore, the use of the more general definition of the shale (as discussed earlier), rather than a specific rock type based on a lithologic or mineral-based classification.

In more detail, the term “oil-shale” is actually a misnomer (Boggs, 2009) as the rock unit does not contain oil but rather contains soluble and insoluble chemical compounds, which can be distilled into a hydrocarbon. These compounds commonly do not exceed a total of 25% of the rock material itself. As stated in the current literature, there is no specific lithologic description of the term. For example, Lee (1991) described oil shale as a “shale, rich in organic matter, which when heated or subjected to destruction yields oil or gaseous hydrocarbon.” Yen and Chilingarian (1976) note that oil shales can be classified as “composites” of tightly bound organics and inorganics, as illustrated in Figure 16. Pettijohn (1975) notes that the term oil shale “has been applied to any rock from which substantial quantities of oil can be extracted by heating.” Key in all these discussions is that the rock type itself is not precisely defined, and the “shale” mineral constituents can actually vary from a shale to a limestone, or to a fine-grained sandstone (Altun et al., 2006).

A similar observation applies to shale plays in general. In describing units as part of gas-bearing shales, Jarvie (2012) noted that a general classification scheme for these systems includes the aspects of “gas type, organic richness, thermal maturity, and juxtaposition of organic-lean, nonclay lithofacies,” without reference to rock type. This can be observed in mineralogical analyses shown in the literature. For example, examining the mineral composition of Barnett Shale samples, the composition of the play unit can vary widely and the samples do not readily correspond to the lithological understanding of a typical “shale” (Figure 17).

35 Petroleum engineering is defined here as the engineering field concerned with production of hydrocarbons, which can be either crude oil or natural gas.
Source: Modified from Altun et al. (2006), based on Yen and Chilingarian (1976).

Note: The inorganic matrix is not defined in detail.

Figure 16: Example of oil shale characterization.
Review of the Effects of CO$_2$ on Very-Fine-Grained Sedimentary Rock/Shale - Part I: Problem Definition

**Figure 17:** Comparison of the range of Barnett shale mineral content with more typical shales.

Note: Clay Minerals Line; observation that most producing shale plays contain less than 50% clay minerals (e.g., Passey et al., 2010).
This is also demonstrated for Eagleford Shale by Passey (2010). It is observed that the clay mineral content of the producing units of the shale plays typically contain less than 40% or 50% of clay minerals (e.g., Britt and Schoeffler, 2009; Passey et al., 2010; Tutuncu, 2012; De Silva et al., 2015). This content distribution indicates that these producing units are not clay-rich (like a typical civil engineering “shale”), but tend to contain more-limited amounts of clay minerals. Testing would also suggest that that the producing shales have higher static moduli, apparently greater than 24 GPa (Britt and Schoeffler, 2009), indicating values at the upper end of “hard shales” in Figure 13.

This general use of the term shale can also further confuse the understanding of specific operational issues. In drilling to depth to intersect the production horizons in shale plays, operations often encounter problems such as borehole collapse and swelling zones (e.g., Chenevert, 1998; Wilson and Wilson, 2014). These problems occur in overlying (nonproducing) shale units, and hence, frequently “shales” are identified as a problem rock. But as these overlying units are not typically sampled, the engineer may be limited to the property data of producing shale, which are unrepresentative of the problem units. This can give rise to the petroleum engineer apparently questioning if shales can swell (e.g., Santarelli and Carminati, 1995), contradicting the common knowledge of the civil engineer.

To summarize, in petroleum engineering and natural gas literature, the term shale is not a lithologic unit but rather represents a catchall term for very-fine-grained sedimentary units. It is part of a formation name when discussing shale plays. Thereby, the term can give rise to misunderstandings with other technical fields.

3.7 LIMITATIONS IN CLASSIFICATION AND RECOMMENDATIONS

3.7.1 Limitations of Current Classification Systems

Upon review of the foregoing, the following observations are made:

- The term “shale” is defined and used differently by various professionals, and such is at best a generalized term for very-fine-grained sedimentary rock, and at worst a catchall, and therefore, the term should never be used without further description.

- There is no accepted standard for the lithographic description of very-fine-grained sedimentary rock, especially silt-size and clay-size particles. A general term of “mudstone,” appears to be more accepted for these materials.

- The lithographic description of very-fine-grained rock, while proving useful in identifying stratification in the field and assisting in geologic analyses, is ill suited for understanding the behavior of these units. In contrast to sandstone, the behavior of these units is not characterized by particle size, but rather is dominated by the mineral

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36 It is also suggested from examined data that for shale plays having greater than 50% clay mineral content, the carbonate content of producing units appears to is less than about 20% (i.e., there is a space in the upper right of the ternary diagram as shown).
constituents and the micro- and macro-fabric of the unit. In addition, de-aggregating the rock material is problematic especially for cemented units.

- In classifying a rock material based on mineralogy, the aspect of the type of clay mineral constituents is often not defined, and the specific type of clay mineral plays a controlling role on material response, especially swell/contraction.

- The distinction of clay mineral size of less than 2 or 3 µm is not applicable to shales due to the effects of lithification and clay mineral. Recent studies have demonstrated that the clay minerals in shales are often present as clay stacks which may range in size up to 150 µm (Seedsman, 1987).

- Engineering classification systems provide a method of quantifying response, but are not descriptive of the various aspects of the material and rely in part on varying lithographic descriptions. In addition, the often-employed index testing from soil mechanics destroys the cementation and the structure of rock material, which can give rise to false conclusions; for example, a well-cemented unit will not swell despite having a high plasticity index.

- In engineering classification, there is a focus on the durability of the material, i.e., the resistance to breakdown due to wetting and drying cycles as measured in slake-durability tests. This appears to be an indirect method to assess the fabric and cementation of the material, but no correlations with swell have been identified.

- The classification of oil- and gas-producing units as “shales” can lead to confusion, as many such geologic units are far from being a “typical” shale.

- The aspects of fabric and to some degree, the anisotropy in response is not addressed by many classification systems and is a major consideration in the behavior of these materials (e.g., O’Brien and Slatt, 1990). Microfabric variations are seldom discussed in technical descriptions.

- When considering shales, there is a focus on the microfabric of the material, but the macrofabric also contributes to the performance of the rock unit in the field. Zones of transverse permeability due to gradation changes/bedding are not included in classifications and the near-vertical fracturing is often not described.

- Finally, aspects of time-dependent response are not included in any classification system.

### 3.7.2 Recommendations for Future Work

It is suggested that several “reference shales” be identified and selected for further study. Rather than employing a single classification system for defining these shales, a more comprehensive approach should be utilized including mineralogy, description of clay content (including individual clay mineral types), engineering testing (including anisotropy), and a description of micro-scale and macro-scale discontinuities (together with a X-ray examinations) be performed on each reference rock unit. Variability with depth and areal extent should also be included in the study.

The type of testing employed would be identified based on a consensus of various experts in the field, who would identify the type of testing, and methods to be employed and the required documentation of a shale. This study may also require specialized sampling methods and
drilling. Collecting samples from near-surface would require care; for example, samples from quarries would need to be sampled at some depth, as near-surface units would be subjected to weathering and related mineral alteration. Also, sample disturbance (as from drying in storage) is a major concern, and re-establishing pressure conditions at depth should also be considered in testing.

Given the importance of shale plays, it is also suggested that one or more of the producing units be examined. It is noted that various data for these units exist, but the data are uncorrelated and only general trends can be identified with current data. Further, one or more troublesome rock units from above the producing horizon should also be included in the study to provide a contrast.

A similar concept was proposed by Underwood (1967) to study shales. He noted that such a study may take several years, but in view of the fact that shales constitute so much of the subsurface, it would provide a solid foundation for understanding these very-fine-grained clastic sedimentary rocks for engineering design, something that is lacking at present. In addition, it would provide a substantial benefit to a wide-range of technical areas ranging from foundation engineering to petroleum production to carbon storage.

3.7.3 Proposed Shale and Mudstone Terminology

To provide a research basis for describing “shale”, a more detailed definition is proposed. It incorporates aspects of both an engineering classification and a lithological definition. As discussions of swell in this report will focus on physiochemical response of clay minerals, consideration of shale is directed here to those rock types with significant clay mineral content (as in the specific definition). It must also be quantitative to allow the researcher or engineer to readily identify what the rock type is under consideration. Lastly, this hybrid definition (as in the general definition) does not require that the rock unit visibly exhibit a fissile nature and assumes a size definition of soil “fines” from sedimentology (Wentworth, 1922).

The following definition is constructed:

**Research Shale:** A clastic sedimentary rock, with a predominant (greater than 50% by volume) grain size of less than 0.063 mm and containing a significant content (greater than 40% by weight) of clay minerals (i.e., layer silicates), and a lower carbonate content (less than 30%). Other constituents can include quartz, chert, felspars, iron and aluminum oxides, and organic matter. The iron oxide content is specified as less than 12%\(^{37}\). The amount of organic matter is typically low, on the order of 1%, but in some horizons may contain substantial amounts (10% or more). The rock fabric exhibits lithification due to compaction and may be cemented as well. Also, the rock fabric is typically transversely anisotropic (i.e., layered) due to depositional processes and the matrix may contain larger clasts, discontinuities and stratification such as bedding and lamina, as well as other heterogeneities, making the rock at times, fissile or laminated. On a laboratory scale, the rock matrix has a minimum uniaxial compressive strength of 0.6 MPa.

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\(^{37}\) This excludes highly ferrous mudstones (such as “ironstones”); a 15% content of iron oxide can be used to define an ironstone as discussed by Pettijohn (1975).
It is understood that this definition of shale will conflict with various uses of the word in the literature\(^{38}\), but provides some basis for systematically evaluating the rock type on the issue of swell. It encompasses the definition of typical shale based on mineralogical content shown in Figure 9, but covers a larger segment of the ternary diagram. Further, it does require testing to determine mineral content and strength, and does not lend itself to visual classification alone.

To describe fine-grained sedimentary rocks in general, the term, “mudstone” is employed in this report, in accordance with recent trends in lithologic terminology. Explicitly, the definition of mudstone is:

**Mudstone\(^{39}\):** A clastic sedimentary rock, with a predominant (> 50%) grain size of less than 0.063 mm. Constituents can include clay minerals, quartz, chert, felspars, carbonates, metal oxides, and organic matter. On a lab scale, the rock matrix has a uniaxial compressive strength of 0.6 MPa or more.

The terms are used in this manner to provide a clear, comprehensive, and scientifically sound, basis for research into what is fundamentally a complex material that is not well understood.

### 3.7.4 Terminology for Scale-Related Descriptors

For the description of rock fabric, it is often necessary to use general terms related to the scale of the item in question. The distinction between what is microfabric and macrofabric, or what is lab scale versus microscopic can be confusing. Lacking a clear, accepted definition in the literature, an arbitrary set of scale-related terms is defined in Figure 19.

The boundaries are consistent with current technical definitions in the literature. For example, the scale defines the boundary between sand-size and silt-size grains at 63 μm, which is approximately at the boundary for definition of size with the unaided eye and is the boundary for particle size of the fines as defined by the International Organization for Standardization (ISO 14688, ISO 14689). The lab scale is defined by typical core size (translating to roughly 1 to 8 in. in diameter), and the bench scale is based on the dimensions of larger laboratory equipment.

\(^{38}\) Using the foregoing classifications, the defined “shale” encompasses various terms as claystone, argillaceous mudstone, physil claystone, clayshale, rock-like shale, soil-like shale, or soft or hard shale.

\(^{39}\) Alternatively, a term “microstone” is proposed for consideration, similar to the grain size designation implicit in the term “sandstone” (i.e. the grain size followed by –stone). This alternative is proposed as the term, “mudstone” can have a negative strength connotation in engineering. While perhaps awkward, this term has the advantage that it does not overlap with terminology previously used in lithologic classification systems.
Note:

a The iron oxide content is specified to be less than 12% of the total weight, as part of the quartz, feldspar and other components category.

b This definition of shale is focused on a material that can swell, and therefore a significant clay mineral content is specified, together with a reduced carbonate content.

Figure 18: Mineralogy of defined research shale.
Note: The clay-size boundary is shown as 2 μm from ISO 14688-1:2002; others define the boundary at 4 μm, e.g., Wentworth (1922). Actual clay mineral particles in shales may substantially exceed these boundaries due to lithification processes.

Figure 19: Definition of scale terminology.
4. CONCLUSIONS AND RECOMMENDATIONS

A review of available literature was conducted to provide a basis for a review of the effects of CO₂ on shale, focusing on two topics: (1) a review of current processes and environmental concerns that use (or are planning to use) CO₂ in the subsurface, as a basis of identifying expected subsurface conditions; and (2) a review of classification methods in order to clearly define the term shale and describe very fine-grained sedimentary rock.

Conclusions of the review are:

1. Carbon dioxide is currently being used in a variety of subsurface activities over a range of in situ conditions. All of these activities can give rise to complex interactions of carbon dioxide, in situ fluids and the rock mass.

2. Under the wide range of in situ conditions for identified processes, the CO₂ phase characteristics will change depending on pressure/temperature conditions. Therefore, various CO₂ phases (gas, liquid and supercritical) need to be considered in evaluating CO₂ in situ response.

3. The rock fabric, especially the (large-scale) macrofabric, is often not well defined in most applications, but it can have major impacts on flow and in the utilization and ultimate success of the specific processes.

4. The term “shale” is defined and used differently by various professionals, and as such it is at best a generalized term for very-fine-grained sedimentary rock, and at worst, it is a catchall, and therefore, technically meaningless. The term shale should never be used without further description, including a detailed analysis of the amount of clay minerals and other content, quantification of the type of clay minerals present, and a detailed description of the microfabric (and macrofabric, if possible).

5. There is no accepted standard for the lithographic description of very-fine-grained sedimentary rock, especially for silt-size and clay-size particles. The term of “mudstone,” appears to be more accepted by the technical community as a general category for these materials. The term shale is generally not used in recent classification methods.

6. The description of oil- and gas-producing units as “shales” can lead to confusion, as many such geologic units are far from being a “typical” shale, i.e., the units are not generally argillaceous.

7. The macrofabric of shale is important to understanding behavior for any process, yet is rarely considered. The microfabric is also rarely described in detail.

8. Based on this review, a revised definition of shale is proposed for CCS community interested in quantifying shale and CO₂ interactions; the material is labeled as a “research shale” (Figure 18).

9. To clarify the array of scale-related terminology in this study, a size-based series of terms is provided (Figure 19).
To provide a more comprehensive basis for the understanding of shales, the following action is recommended:

- Identification and testing of several “reference shales” to provide a basis for engineering analyses. The reference units would be subjected to an array of tests as part of a more comprehensive classification approach, and include testing to quantify the clay mineralogy and content (including individual clay mineral types), engineering testing (including anisotropy), and a description of micro-scale and macro-scale discontinuities (together with a X-ray examinations). An assessment of variability with depth and areal extent should also be included in the study.
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APPENDIX: ADDITIONAL CLASSIFICATION SYSTEMS

A.1. GENERAL

Some additional figures on classification systems are provided in this appendix, which are informative but not widely available and not discussed in main body of report.

Füchtbauer (1959) developed a classification system based on mineral content, which is still frequently utilized in European literature, in particular for nuclear waste analyses. Figure A1 illustrates the main categories from the author as translated into English. Figure A2 provides the full set of 25 categories shown by Füchtbauer et al. (1988).

Larese and Heald (1977) utilized a lithological classification system (based on grain size), as illustrated in Figure A3. The system correlates directly with the Shepherd (1954) system developed for soils. Shepherd examined several classification systems and selected his recommended approach based on a survey of various experts in the field.

A relatively simple classification system based on mineral content is attributed to Allix et al. (2010) and is shown in Figure A4. The system is developed for use in the petroleum industry and many shale plays are defined as siliceous mudstones, as illustrated by Gamero-Diaz et al. (2012).

Another classification system is also proposed to distinguish between “sealing shales,” which have a higher clay mineral content and "brittle shales" with less clay minerals (Bourg, 2015, Figure 4). The sealing shale is more optimal for fractures that heal or close with time as part of radioactive waste storage. A sealing shale requires at least a 33% clay mineral content, as shown in Figure A5.

An attempt was also made to classify shales with respect to swell potential based on mineralogy (Barla, 1999). Three categories of swell potential were identified based on data from stiff clay, claystones and clay shales, as shown in Figure A6.
Source: Modified from Füchtbauer (1959) (see also Füchtbauer et al., 1988); Categories grouped, and terms translated from German (see Koroleva et al., 2009).

Figure A1: General Mineralogy Classification System from Füchtbauer et al. (1988).
Figure A2: Detailed Mineralogy Classification System from Füchtbauer et al. (1959).
Review of the Effects of CO₂ on Very-Fine-Grained Sedimentary Rock/Shale - Part I: Problem Definition

Figure A3: Grain-Size Based Classification System Shown by Larese and Heald (1977).

Source: Larese and Heald (1977); system correlates with Shepherd (1954) for unconsolidated sediments (soils).
Review of the Effects of CO₂ on Very-Fine-Grained Sedimentary Rock/Shale - Part I: Problem Definition

Figure A4: Mineralogy Classification System from Allix (2010).

Source: Attributed to Allix et al. (2010), but figure not shown in source; figure is shown by Gamero-Diaz et al. (2012).
Fine-Grained Clastic Sedimentary Unit
(Predominate Grain Size < 0.0625 mm)

Sealing Shales

Brittle Shales

Clay Minerals & Organics

Carbonates


Figure A5: Definition of Sealing Shale and Brittle Shale by Bourg (2015).
Source: Modified from Barla (1999).

Note: Proposed correlation based on data from Cameva Clay, Terravecchia Claystone and Varicolori Clay Shale from Sicily.

Figure A6: Classification of Swelling Potential of a Stiff Clay Based on Mineralogy from Barla (1999).
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