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INCORPORATING CAPILLARY ENTRY PRESSURE MEASUREMENTS INTO EVALUATIONS OF STORAGE PERMANENCE FOR PERMITTING CLASS VI INJECTION WELLS

White Paper

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EXECUTIVE SUMMARY

The injection of carbon dioxide (CO_2) for permanent geologic storage requires the approval of a Class VI permit application by state or federal regulatory authorities. Among the permitting requirements, data must be provided on the capillary entry pressure of the injection and confining zones. In geologic media, capillary entry pressure is defined as the lowest pressure required to begin to displace in situ formation fluids (the wetting phase) during the injection of a non-wetting-phase fluid (CO_2). For confining zones that immediately overly the injection zone (hereafter “cap rock”), capillary entry pressure provides an indication of the maximum upward CO_2 force that can be held within the injection zone before CO_2 starts to permeate the confining zone.

Three main laboratory test methods are commonly used for determining capillary entry pressure: i) centrifuge method, ii) semipermeable membrane (porous plate) method, and iii) mercury–air (high-pressure mercury injection [HPMI]) method. For geologic storage of CO_2, HPMI is the most common method for measuring capillary entry pressures, especially for geologic materials with small pore sizes like those found in cap rocks.

There is no absolute capillary entry pressure number that, in and of itself, can be deemed “good” or “bad.” Instead, the capillary entry pressure must be evaluated in the context of the predicted upward CO_2 force at the injection zone–cap rock interface. A workflow is presented herein that provides a screening-level assessment method that uses capillary entry pressure measurements to estimate cap rock sealing capacity and evaluate permanence for the long-term storage of CO_2. Inputs to this workflow include i) pressure and temperature of the injection zone, ii) formation fluid and CO_2 density in the injection zone, iii) column height of CO_2 in the injection zone, and iv) capillary entry pressure of the injection zone and cap rock. The maximum height of CO_2 that a cap rock can safely seal is determined using the injection zone and cap rock capillary entry pressures and density differences between formation fluid and CO_2. The sealing capacity of the cap rock can be evaluated by calculating the ratio of capillary entry pressure to the buoyant pressure of the CO_2 column in the injection zone. Ratios greater than 1 represent greater cap rock sealing capacity. This workflow permits CO_2 storage project owners or operators to verify that the capillary entry pressure exceeds pressure increases expected from the buoyancy-driven accumulation of CO_2 in the injection zone, as recommended by the U.S. Environmental Protection Agency.[1]

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[1] U.S. Environmental Protection Agency, 2013, Underground injection control (UIC) program Class VI implementation manual for UIC program directors: EPA 816-R-13-004.

This document i) provides an overview of capillary entry pressure, ii) summarizes laboratory methods for determining capillary entry pressure, and iii) provides examples and interpretations of capillary entry pressure data for evaluating cap rocks and storage permanence for permitting Class VI injection wells.

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INCORPORATING CAPILLARY ENTRY PRESSURE MEASUREMENTS INTO EVALUATIONS OF STORAGE PERMANENCE FOR PERMITTING CLASS VI INJECTION WELLS

INTRODUCTION

Carbon capture and storage (CCS) is a process that captures carbon dioxide (CO_2) from an anthropogenic point source, preventing its release to the atmosphere, and injects the captured CO_2 via one or more injection wells into a deep geologic reservoir for permanent storage. CCS is a key technology option to mitigate CO_2 emissions while allowing the full range of economic and societal benefits to be realized from the continued use of fossil fuels. The Plains CO_2 Reduction (PCOR) Partnership Initiative, funded by the U.S. Department of Energy (DOE), the North Dakota Industrial Commission (NDIC) Oil and Gas Research Program and Lignite Research Council, and participating member organizations, is accelerating the deployment of CCS in the PCOR Partnership region. The PCOR Partnership region covers the central interior of North America and includes ten U.S. states (Alaska, Iowa, Minnesota, Missouri, Montana, Nebraska, North Dakota, South Dakota, Wisconsin, and Wyoming) and four Canadian provinces (Alberta, British Columbia, Manitoba, and Saskatchewan). The Energy & Environmental Research Center (EERC) at the University of North Dakota leads the PCOR Partnership Initiative, with support from the University of Wyoming and the University of Alaska Fairbanks.

The injection of CO_2 for permanent geologic storage requires the approval of a Class VI permit application by state or federal regulatory authorities.[2] Among the list of permitting requirements, data must be provided on the capillary entry pressure of the injection and confining zones (U.S. Environmental Protection Agency, 2013).[3] In geologic media, capillary entry pressure

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[2] In the United States, the U.S. Environmental Protection Agency (EPA) regulates the construction, operation, permitting, and closure of injection wells used to place fluids underground for storage. The federal regulations for the underground injection control (UIC) program are found in Title 40 of the Code of Federal Regulations (CFR) (Parts 124, 144, 145, 146, and 147). The Safe Drinking Water Act (SDWA) establishes requirements and provisions for the UIC program. Regulations for CCS fall under the Class VI rule of the UIC program – Wells Used for Geologic Sequestration of CO_2. Two states—North Dakota and Wyoming—have primary enforcement authority, or primacy (recognized by EPA), under the SDWA to implement a UIC program for Class VI injection wells located within their states, except within Indian lands. The remaining 48 states must secure EPA approval of all Class VI injection well permits.

[3] The *injection zone* is defined as a geologic formation, group of formations, or part of a formation that is of sufficient areal extent, thickness, porosity, and permeability to receive CO_2 through a well or wells associated with a geologic sequestration project (North Dakota Administrative Code [NDAC] Chapter 43-05-01, Geologic Storage of Carbon Dioxide, Section 43-05-01-01, Definitions). The injection zone is synonymous with the terms "storage unit" and "storage reservoir" (International Organization for Standardization, 2017). *Confining zones* refer to a geologic formation, group of formations, or part of a formation stratigraphically overlying the injection zone that acts as a barrier to fluid movement (NDAC Chapter 43-05-01, Geologic Storage of Carbon Dioxide, Section 43-05-01-01, Definitions). Confining zones are synonymous with the term "confining strata" and when describing the confining zone immediately overlying the injection zone are also called the "primary seal" or "cap rock" (International Organization for Standardization, 2017).

is defined as the lowest pressure required to begin to displace in situ formation fluids (the wetting phase) during the injection of a non-wetting-phase fluid (CO_2) (Espinoza and Santamarina, 2017). Capillary entry pressure provides an understanding of the ability for CO_2 to be safely injected into the fluid-filled injection zone and is therefore a critical input for the hydrogeologic characterization of the injection zone and the modeling and simulation of the injected CO_2 (International Organization for Standardization, 2017). Capillary entry pressure also provides an indication of the maximum upward CO_2 force that can be held within the injection zone before CO_2 starts to permeate the confining zone immediately overlying the injection zone (hereafter "cap rock"). The remainder of this report i) provides an overview of capillary entry pressure, ii) summarizes laboratory methods for determining capillary entry pressure, and iii) provides examples and interpretations of capillary entry pressure data for evaluating cap rocks and storage permanence for permitting Class VI injection wells.

CAPILLARY ENTRY PRESSURE OVERVIEW

Figure 1 illustrates CO_2 injected into an idealized injection zone and the CO_2 movement and displacement of in situ formation fluids. During injection, density differences between the less dense CO_2 and the denser formation fluids cause CO_2 to migrate to the top of the injection zone and contact the cap rock (buoyancy drive). In addition, viscosity differences between the less viscous CO_2 and the more viscous formation fluids will cause the CO_2 to migrate laterally within the injection zone (mobility). The combination of these forces results in a typical profile of the CO_2 plume in the injection zone where the CO_2 lateral extent is greatest at the cap rock–injection zone interface and the CO_2 column height (thickness) is greatest near the injection well (Figure 1A) (Buckly and Leverett, 1942; Nordbotten and others, 2005; Vilarrasa and others, 2013).

CO_2 is less dense than formation water at typical injection zone pressure and temperature conditions.[4] Consequently, stored CO_2 creates a pressure difference (buoyancy drive) at the cap rock–injection zone interface that is proportional to the column height of the CO_2 in the injection zone and the difference in mass density between the formation fluid and the stored CO_2 (Equation 1) (Weyer, 1978; Dandekar, 2013; Espinoza and Santamarina, 2017).

$$\Delta P = (\rho_w - \rho_{CO2})\, g\, h \times (1.45 \times 10^{-4}) \qquad \text{[Eq. 1]}$$

Where:

ΔP is the pressure difference (buoyancy drive) [psi].
ρ_w is the density of the formation fluid at reservoir pressure and temperature conditions [kg/m^3].
ρ_{CO2} is the density of the CO_2 at reservoir pressure and temperature conditions [kg/m^3].
g is the acceleration due to gravity [9.81 m/s^2].
h is the column height of CO_2 [m].
1.45×10^{-4} is a conversion factor from pascals to psi.

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[4] CO_2 is in a supercritical state in injection zones at or above the temperature and pressure thresholds that are necessary for CCS projects, i.e., 88°F (31.1°C) and 1070 psi (7.38 Mpa), respectively (Bachu, 2003).

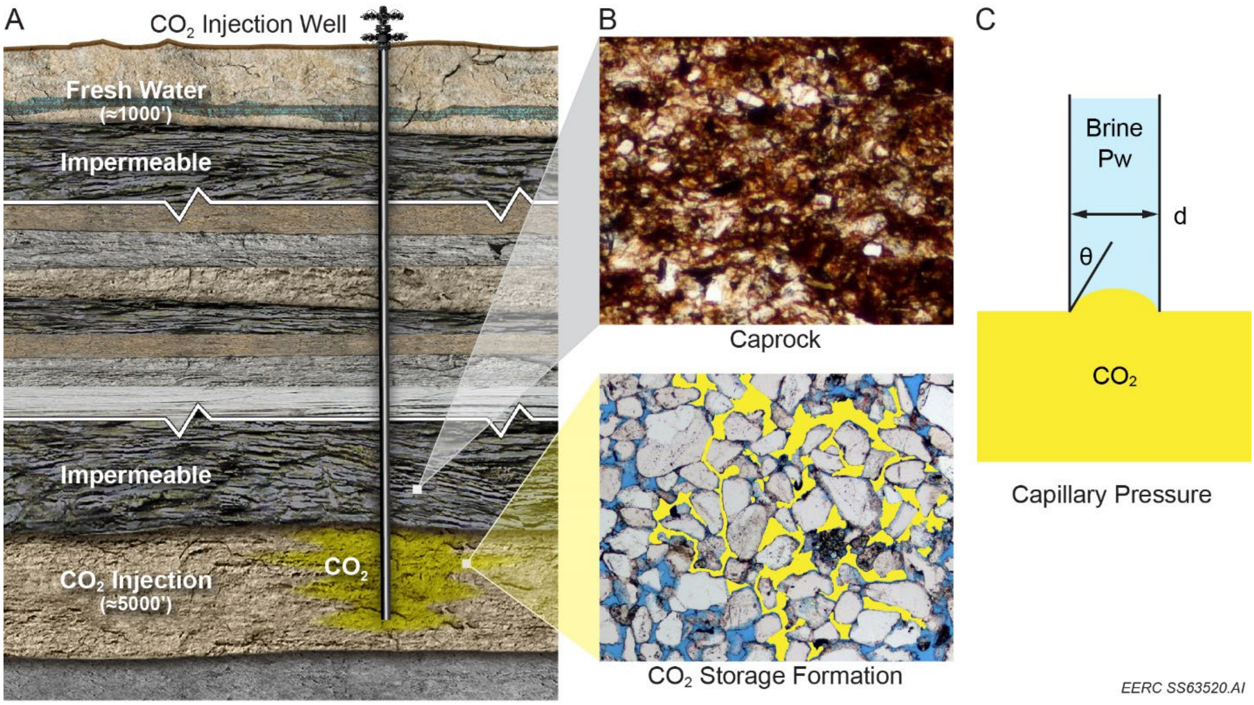

Figure 1. Illustration of CO_2 injection into an injection zone overlain by a cap rock and successive geologic layers to the ground surface (A), buoyant forces moving CO_2 through the injection zone (CO_2 storage formation) and against the cap rock (B), and CO_2 in a capillary tube showing the contact angle formed by the water–CO_2 interface (θ) and the capillary tube diameter (d^*) (C), which is analogous to the rock pore throat diameter.

The cap rock must resist the long-term upward pressure exerted by the CO_2 stored in the injection zone. If the buoyancy drive created by the CO_2 column in the injection zone (ΔP from Equation 1) exceeds the capillary entry pressure, then the sealing integrity of the cap rock could be insufficient. Therefore, in conjunction with many other geological and geomechanical factors, the capillary entry pressure characteristics of the cap rock become an important consideration in the assurance of long-term containment, or permanence, of the CO_2 storage.

Capillary entry pressure is controlled by the combination of the interfacial tension (IFT) between two fluids (CO_2 and formation fluid), wetting characteristics of the two fluids on the pore wall (contact angle), and the pore sizes of the rock. When the pore shape is assumed to be a cylinder (capillary tube, Figure 1B), the capillary entry pressure can be estimated by the Equation 2 (Dandekar, 2013; Espinoza and Santamarina, 2010, 2017).

$$P_c = \frac{2\,\sigma\,cos\theta}{r} \times \,(1.45 \times 10^{-4}) \qquad \text{[Eq. 2]}$$

Where:

P_c is the capillary entry pressure [psi].

σ is the interfacial tension between water and CO_2 [Newtons (N)/m].
θ is the contact angle formed by the water–CO_2 interface on the mineral surface [degrees].
r is the capillary radius (pore throat radius) [m].
1.45×10^{-4} is a conversion factor from N/m^2 (pascals) to psi.

As shown in Equation 2, capillary entry pressure is a function of the adhesion tension ($\sigma\ cos\theta$) and inversely proportional to the pore throat radius (r). The smaller the contact angle, the greater the height of liquid rise in the capillary tube (Figure 1B) and stronger the adhesion tension, leading to higher capillary entry pressure. Conversely, the larger the contact angle (weaker wetting characteristics or adhesion tension), the lower the capillary entry pressure. Pore throat radius is in the denominator; therefore, capillary entry pressure is inversely proportional to the pore throat size—the capillary entry pressure will be lower for large pore throats and higher for small pore throats. Because the injection zones for most deep saline formations are expected to have relatively larger pore throats, fluid displacement occurs at relatively low differential pressures above the initial (preinjection) pressure in the injection zone. Stated differently, the capillary entry pressures for injection zones are relatively low (e.g., less than 50 psi). Conversely, the pore throat sizes in cap rocks are significantly smaller than injection zones; therefore, the capillary entry pressures for cap rocks can be quite high (e.g., greater than 100 psi) and are typically greater than the capillary entry pressures of the injection zones.

Figure 2 illustrates the relationship between pore throat size on the *x*-axis (using mercury saturation as a proxy for pore throat size) and mercury injection pressure on the *y*-axis for a typical curve derived during high-pressure mercury injection (HPMI) laboratory experiments (HPMI is explained in greater detail in the next section). The initial zone near the lower right-hand portion of the figure (S_{Hg} = 0%) represents mercury being injected into and invading the largest pores first with a lower capillary entry pressure. As the mercury fills incrementally smaller pores, moving right to left along the *x*-axis, the mercury injection pressure increases toward the upper left-hand portion of the figure (S_{Hg} = max%). Curves like the one shown in Figure 2 can be used to estimate the capillary entry pressure for different rock samples.

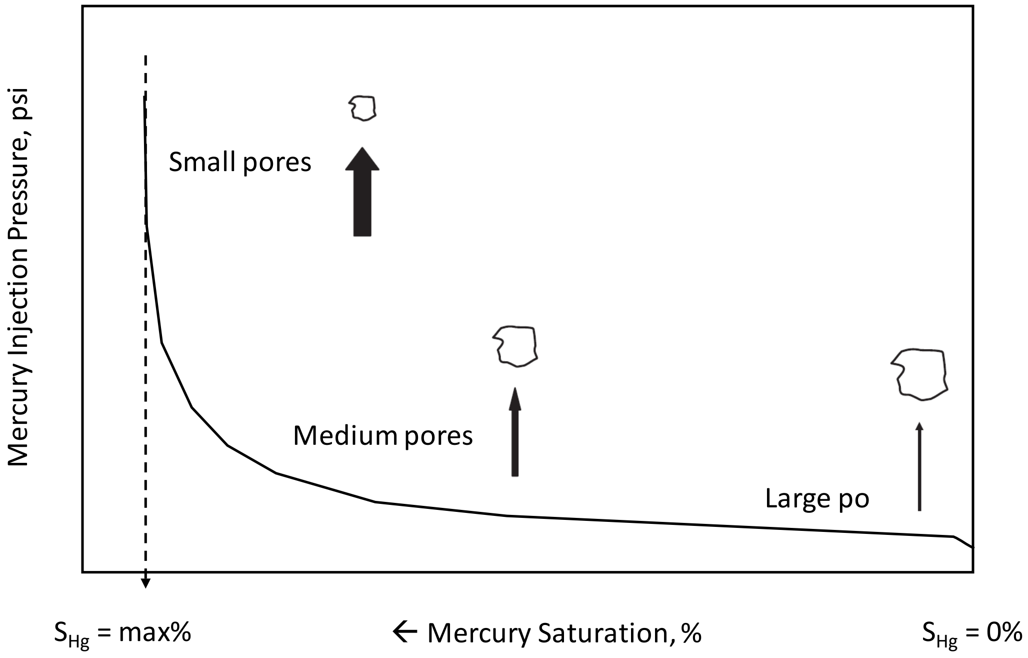

Figure 2. Schematic representation of mercury invasion into large, medium, and small pores, as part of the mercury injection process for measurement of capillary entry pressure, showing the relationship between mercury saturation from 0% to max% (*x*-axis) and mercury injection pressure (*y*-axis) developed from HPMI laboratory experiments (adapted from Dandekar, 2013).

Capillary entry pressure is commonly defined from the minimum pressure required for mercury to imbibe into the pore space. Figure 3 illustrates the influence of pore size and distribution on the measured capillary entry pressure for three rock samples: A) permeable sandstone (injection zone with larger pore size), B) dolomitic sandstone (injection zone with smaller pore size), and C) siltstone (cap rock with small pore size). For the permeable sandstone sample (Figure 3A), the pore throat histogram shows that 94% of the pores had a radius greater than 2.5 µm (mega pores), resulting in a capillary entry pressure of 4 psi and 50% of the pore volume being filled (displaced by the injected mercury) at only 10 psi of injection pressure. For the dolomitic sandstone sample (Figure 3B), the pore throat histogram shows micro- and nano-µm (<0.75 µm)-sized pores dominate the sample and the capillary entry pressure was 200 psi. Nearly 800 psi was required to fill 50% of the pore volume. Lastly, for the siltstone sample (Figure 3C), the pore throat histogram shows that 90% of the pores were in the nano-µm range (<0.10 µm) and the capillary entry pressure was 300 psi. Because of the small pores, the injection pressure needed to fill 50% of this pore space was 9000 psi. Curves like the ones shown in Figure 3 provide site-specific characterization data of the capillary entry pressures for the injection zone and cap rock, which are required inputs for Class VI injection well permits.

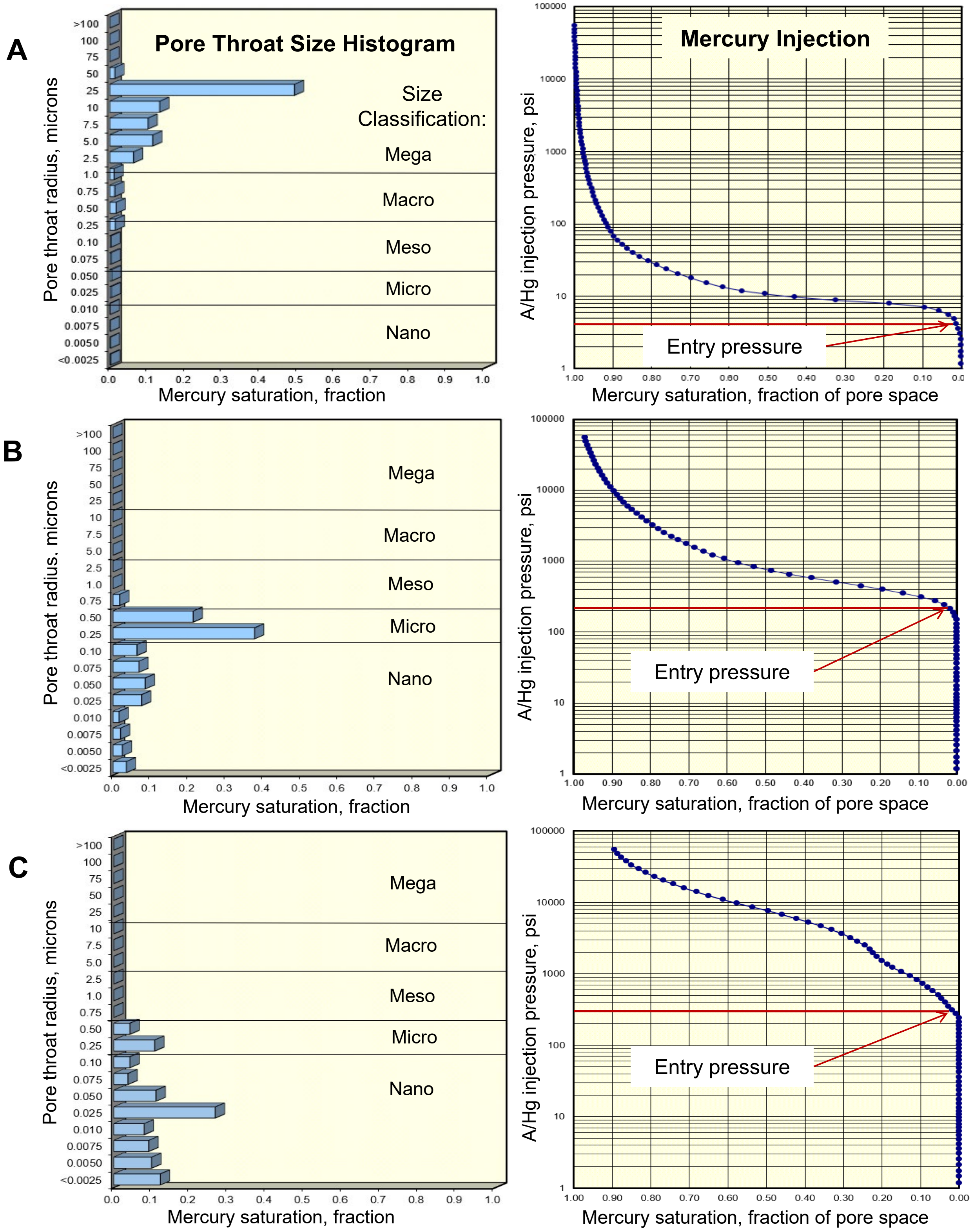

Figure 3. Pore throat size distributions (left column) and corresponding capillary entry pressure curves (right column) obtained from HPMI laboratory experiments for A) permeable sandstone sample, B) dolomitic sandstone sample, and C) siltstone sample (cap rock).

LABORATORY METHODS FOR DETERMINING CAPILLARY ENTRY PRESSURE

Three main laboratory test methods are commonly used for determining capillary entry pressure: i) centrifuge, ii) semipermeable membrane (porous plate), and iii) HPMI (U.S. Environmental Protection Agency, 2013).

Centrifuge Method

In the centrifuge method, a rock core plug (sample) is placed into a centrifuge core holder, which is then rotated at increasingly greater rates (Figure 4). The rotation generates a centrifugal force that is exerted on the core plug. During the centrifuge process, formation fluid is expelled from the core plug and a glass container measures the amount of fluid as it is being expelled (shown as the production vessel and produced fluid in the figure). The method results in a curve that relates rotation speeds with the expelled (or drainage) amounts, which are then used to derive the capillary entry pressure using mathematical equations.

Certain laboratories use fully automated centrifuges with video or photographic data collection systems to establish capillary entry pressure and wetting characteristics. Tests can be run at elevated pressure and temperature conditions. Ultracentrifuges allow capillary entry pressure and saturation characterization of low-permeability rocks; however, ultracentrifuges are the most expensive method and have several disadvantages, such as the creation of unusual stress patterns and saturation regimes (McPhee and others, 2015).

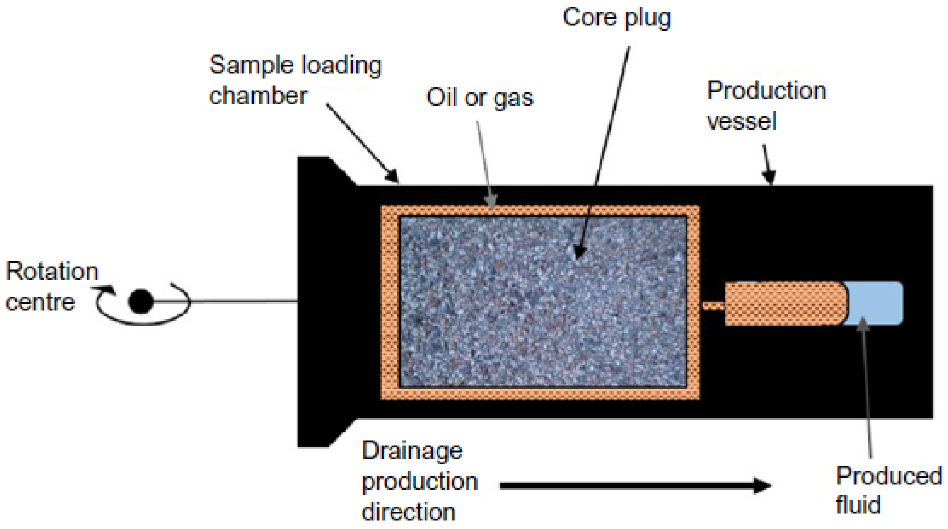

Figure 4. Centrifuge core holder (McPhee and others, 2015).

Semipermeable Membrane (Porous Plate) Method

In the porous plate method, a sample saturated with water is placed on a flat porous plate, which is also saturated with water, and placed inside a gas chamber (Figure 5). Gas is added at increasing pressures, thus displacing the water through the plate. The pressure of the gas represents the capillary entry pressure, and the amount of water expelled from the porous plate is related to the water saturation of the sample.

The porous plate method is accurate for determining capillary entry pressure relationships in fluid–air systems. One of the main disadvantages of the method is the relatively long time required to define a full capillary entry pressure curve. The time is regulated by the rate of formation fluid drainage through the porous plate, which can be time-consuming for cap rock materials that have extremely low permeability. The porous plate method can be done on batch cells or individual cells. The latter is the more expensive approach, as it requires a dedicated core holder for each sample. In addition, the porous plate method is not suitable for unconsolidated samples (McPhee and others, 2015).

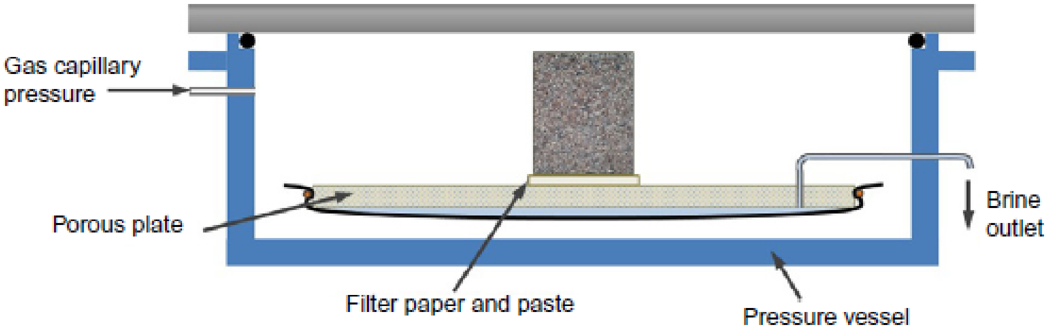

Figure 5. Batch porous plate equipment (ambient) (McPhee and others, 2015).

HPMI Method

In the mercury injection method, a rock core sample is placed into the sample cell and a vacuum-filling apparatus removes air from the cell and pores. This is followed by mercury filling the pores with predetermined increasing pressure steps. During the test, the volume of mercury at each pressure step is recorded. The relationship between the mercury intrusion pressure and the mercury saturation in the core is the capillary pressure curve, which can be used to provide estimates of the capillary entry pressure, pore size distribution, and pore level heterogeneity. The method can be implemented at high pressures—HPMI—for geologic materials with small pore sizes like those found in cap rocks (Figure 6). The mercury injection method is well-suited to irregular rock samples such as cuttings.

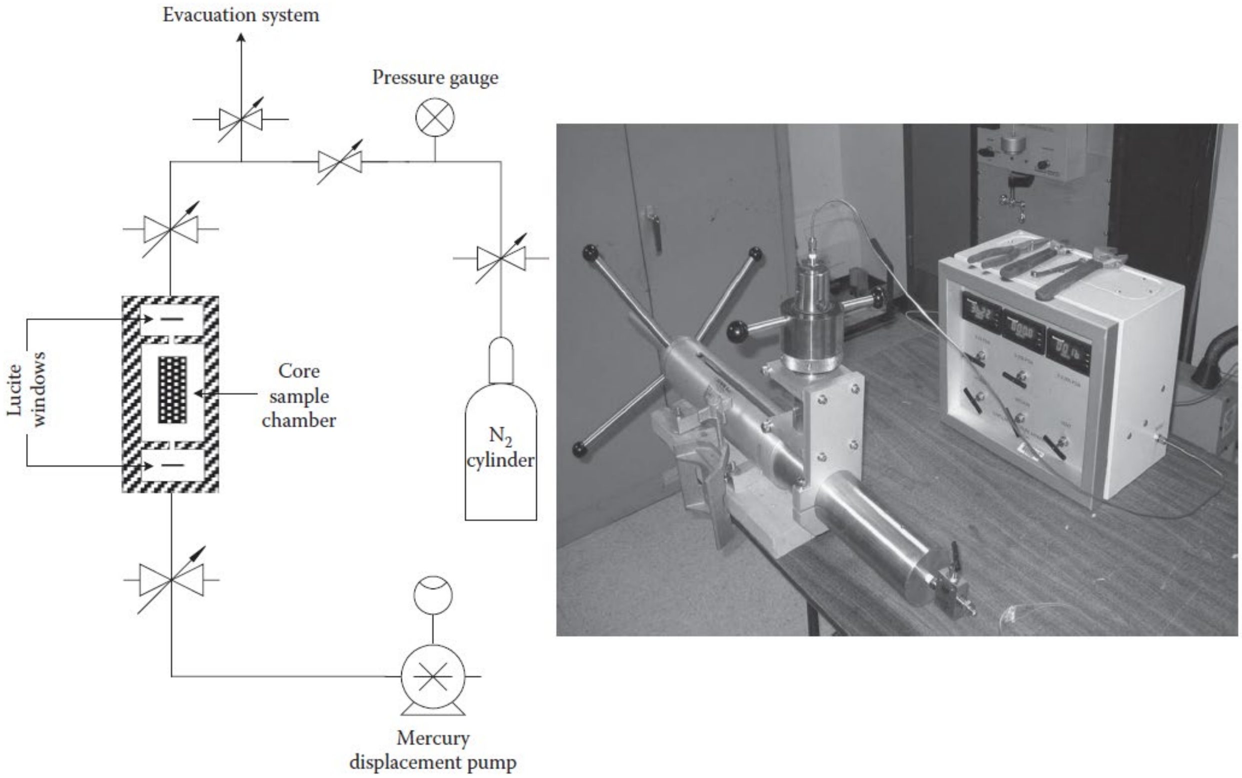

Figure 6. Schematic and photo of a representative HPMI measurement setup (Dandekar, 2013).

The process of injecting mercury and acquiring data is rapid in comparison to other methods for estimating capillary entry pressure, especially for small pore sizes found in cap rocks, making the HPMI method the most common method for estimating the capillary entry pressure of geologic materials for CCS projects, especially for cap rock materials with nano-µm pore sizes. One disadvantage of the method is that it requires a conversion to represent a CO_2-formation fluid system for CCS projects. Also, the test uses relatively small samples; therefore, the results may not be representative for geologic units with significant heterogeneity (McPhee and others, 2015).

The capillary entry pressure obtained from the HPMI test must be converted from a mercury–air system to CO_2–brine system. Equation 3 can be used to convert the capillary pressure using CO_2 and brine contact angle and the interfacial tension for each formation.[5]

$$P_{c_{CO2/brine}} = P_{c_{Hg/air}} \frac{T_{CO2/brine} \cos\theta_{CO2/brine}}{T_{Hg/air} \cos\theta_{Hg/air}} \qquad \text{[Eq. 3]}$$

Where:

$P_{c_{CO2/brine}}$ is the capillary entry pressure for CO_2/brine system [psi].

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[5] The HPMI experiment is conducted on Hg–air. The $T_{CO2/brine}$ and $\theta_{CO2/brine}$ are characteristics of the geologic media and are measured using different experiments—interfacial tension and contact angle measurements, respectively—which use formation fluid (brine), CO_2, and rock discs.

$P_{c_{Hg/air}}$ is the capillary entry pressure for mercury–air system [psi].
$T_{CO2/brine}$ is the CO_2 and brine interfacial tension [N/m].
$T_{Hg/air}$ is the mercury and air interfacial tension [0.485 N/m in this example].
$\theta_{CO2/brine}$ is the contact angle for CO_2–brine–rock system [degrees].
$\theta_{Hg/air}$ is the contact angle for mercury–air–rock system [140° in this example].

Figure 7 shows example HPMI results for three cap rock samples from the PCOR Partnership region, and Table 1 provides an example of the laboratory output. The estimated mercury capillary entry pressures ($P_{c_{Hg/air}}$) for the three cap rock core samples were as follows: black shale (3560 psi), silty shale (828 psi), and muddy siltstone (352 psi). These mercury capillary entry pressures were then converted to CO_2 capillary entry pressures ($P_{c_{CO2/brine}}$) as follows: black shale (1317 psi), silty shale (291 psi), and muddy siltstone (129 psi).

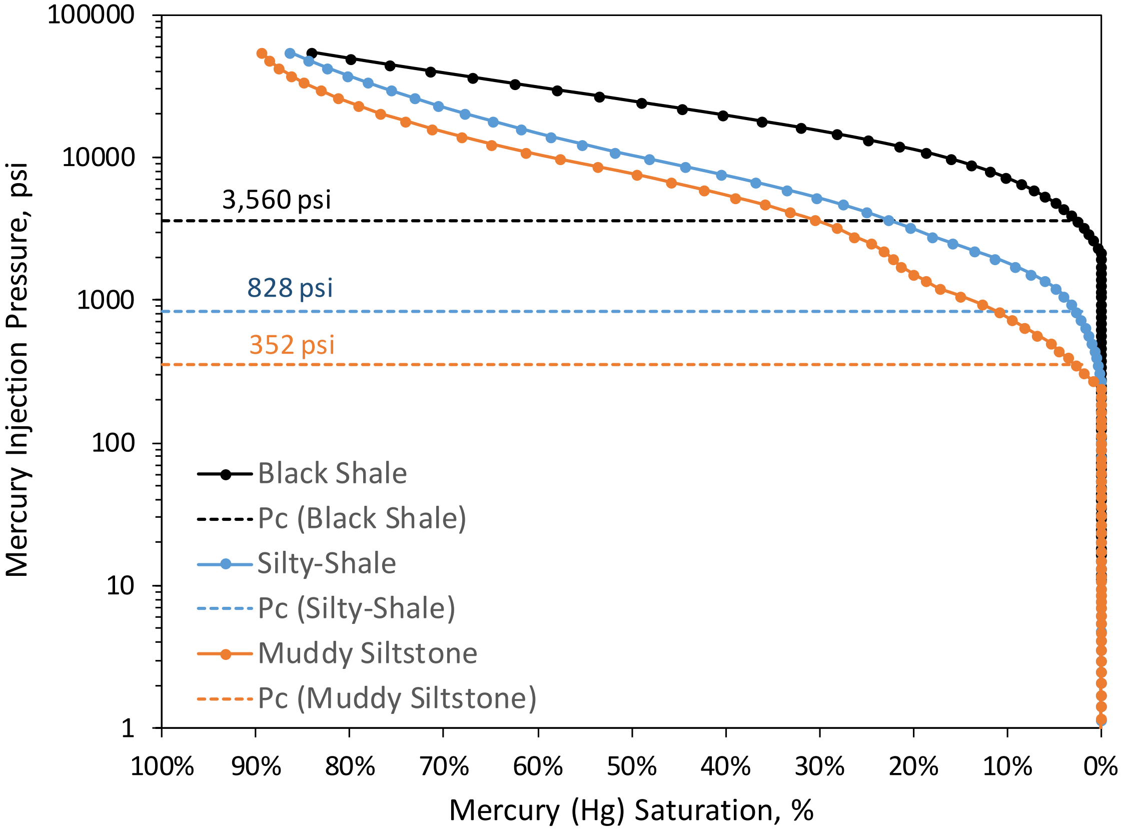

Figure 7. Example HPMI results for three cap rock core samples from the PCOR Partnership region showing saturation–pressure curves and estimated mercury capillary entry pressures ($P_{c_{Hg/air}}$) for a black shale (3560 psi), silty shale (828 psi), and muddy siltstone (352 psi). These mercury values were then converted to CO_2 capillary entry pressures ($P_{c_{CO2/brine}}$) using Equation 3 as follows: black shale (1317 psi), silty shale (291 psi), and muddy siltstone (129 psi).

Table 1. HPMI Results for Three Cap Rock Core Samples from the PCOR Partnership Region Showing Laboratory Results for CO_2–Brine Contact Angle ($\theta_{CO2/brine}$), CO_2–Brine IFT ($T_{CO2/brine}$), Average Pore Size, Mercury Capillary Entry Pressure ($P_{c_{Hg/air}}$), and CO_2 Capillary Entry Pressure ($P_{c_{CO2/brine}}$)

Formation/Lithology	CO_2–Brine Contact Angle ($\theta_{CO2/brine}$), degrees	CO_2–Brine IFT ($T_{CO2/brine}$), mN/m	Average Pore Size, µm	Mercury Entry Pressure ($P_{c_{Hg/air}}$), psi	CO_2 Entry Pressure ($P_{c_{CO2/brine}}$), psi
Formation 1/Black Shale	34.46	35.3	0.0050	3560	1317
Formation 2/Silty Shale	21.61	36.0	0.0075	828	291
Formation 3/Muddy Siltstone	21.72	24.7	0.0250	352	129

USING CAPILLARY ENTRY PRESSURE DATA FOR CAP ROCK EVALUATIONS

As previously discussed, CO_2 from the injection zone can permeate the cap rock when the pressure from the buoyancy drive exceeds the capillary entry pressure of the cap rock, making the capillary entry pressure characteristics of the cap rock an important consideration in the assurance of long-term containment of the stored CO_2 (permanence). This section provides a screening-level assessment method for estimating cap rock sealing capacity for long-term CO_2 storage. The workflow i) uses established equations from the peer-reviewed literature and input values for the parameters of those equations (including capillary entry pressure measurements) and ii) evaluates the cap rock sealing capacity—the ability of the cap rock to resist the upward forces from the stored CO_2 (buoyancy drive).

Step 1 – Estimate Buoyancy Drive

As shown in Equation 1, the formation fluid density (ρ_w) and CO_2 density (ρ_{CO2}) at reservoir pressure and temperature conditions are two important parameters for estimating buoyancy drive, along with the acceleration due to gravity (g), a constant (9.81 m/s^2), and the column height of CO_2 in the injection zone (h). Therefore, the first step in the method is to estimate the buoyancy drive, which requires estimating the i) formation fluid and CO_2 density in the injection zone and ii) column height of CO_2 in the injection zone.

Estimate Formation Fluid and CO_2 Density in the Injection Zone

Formation fluid density can be estimated from temperature, pressure, and salinity using functions such as those developed by Bandilla (2016) based on the brine density solutions described in Haas (1976) and Battistelli and others (1997). Similarly, CO_2 density can be estimated from temperature and pressure using equations of state such as Duan and others (1992) or Span and Wagner (1996). These methods are described in detail in the supporting information of Burton-Kelly and others (2021) and are beyond the scope of the current document. Additionally, the National Institute of Standards and Technology (NIST) has online tools available for estimating formation fluid and CO_2 density (National Institute of Standards and Technology, 2022). Assuming pressure gradients between 0.433 psi/ft (freshwater) and 0.480 psi/ft (representative of some injection zones in North Dakota) and temperature gradients of 0.016°F/ft with a surface offset of 43°F (representative of some regions in North Dakota), the pressure, temperature, formation fluid density (assuming 50,000. 100,000, or 200,000 ppm salinity), and CO_2 density estimated as a function of depth are shown in Figure 8. For the example shown in Figure 8, the top of the injection zone is located at 5000 ft and the formation thickness is 300 ft (i.e., the bottom of the injection zone is located at 5300 ft), as shown by the brown dashed box. The predicted pressure and temperature at the top of the injection zone are estimated to be 2181–2415 psi and 123°F, respectively, resulting in an estimated formation fluid density for 100,000 ppm of 1063 kg/m^3 (ρ_w) and an estimated CO_2 density of 699–732 kg/m^3 (ρ_{CO2}).

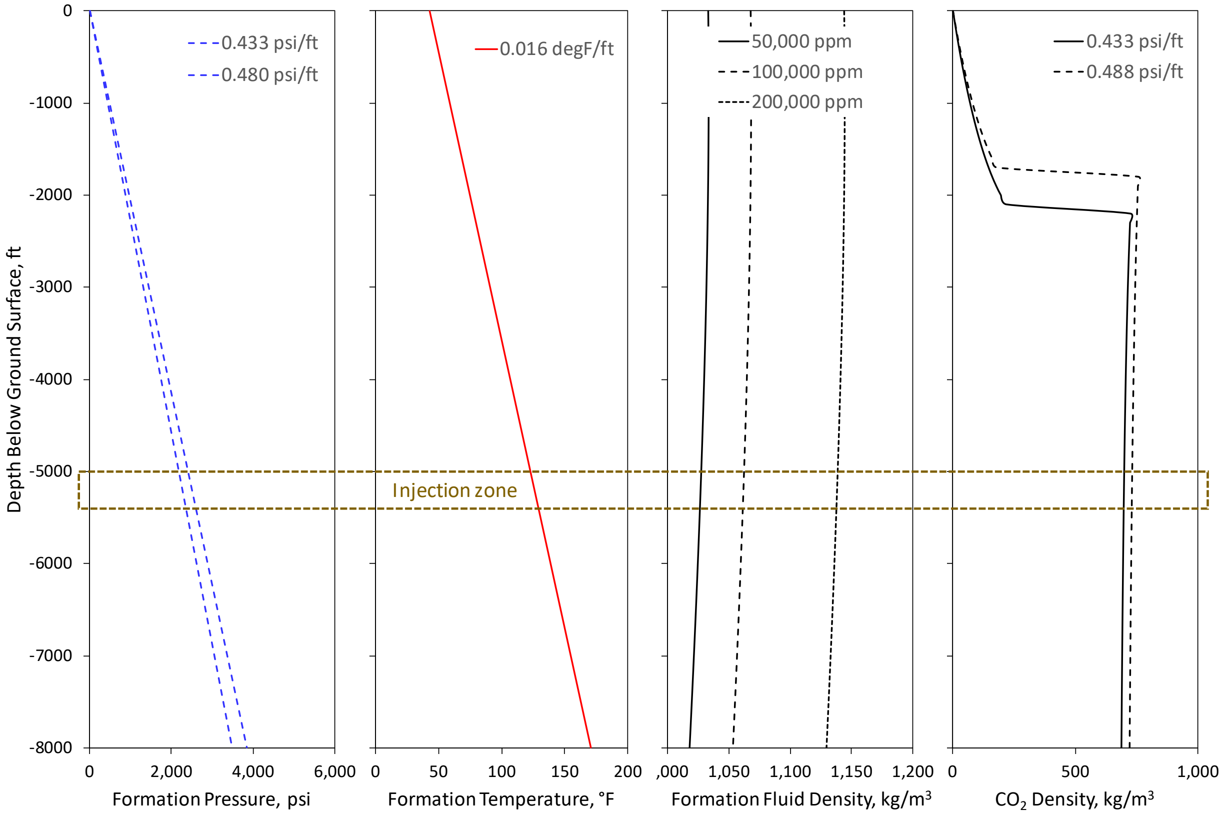

Figure 8. Estimated formation pressure (left panel), temperature (second panel), fluid density (third panel), and CO_2 density (right panel) as a function of depth using the assumptions described in the text. For the example described in the text, the top of the injection zone is located at 5000 ft and the thickness is 300 ft (i.e., the bottom of the injection zone is located at 5300 ft), as shown by the brown dashed box.

Estimate Column Height of CO_2 in the Injection Zone

Near the injection well, the column height of CO_2 in the injection zone could theoretically extend throughout the entire formation thickness (300 ft, in this example). However, while the CO_2 plume thickness near the injection well progressively increases with time as CO_2 is injected, the

CO_2 remains in the upper part of the injection zone because of buoyancy (density differences between formation fluid and CO_2); therefore, CO_2 is not necessarily present throughout the whole thickness of the injection zone during the entire period of CO_2 injection. This CO_2 plume behavior in the injection zone has been described from theory using fundamental equations for multiphase fluid flow (e.g., Vilarrasa and others, 2013) and consistent with numerical reservoir simulation (Figure 9). Therefore, for the example described here, the column height of CO_2 was estimated from 10% of the formation thickness (0.1 × 300 ft = 30 ft [9.1 m]) to 90% of the formation thickness (0.9 × 300 ft = 270 ft [82.3 m]) to explore a range of buoyancy drive from the CO_2 plume fringe toward the injection well, respectively.

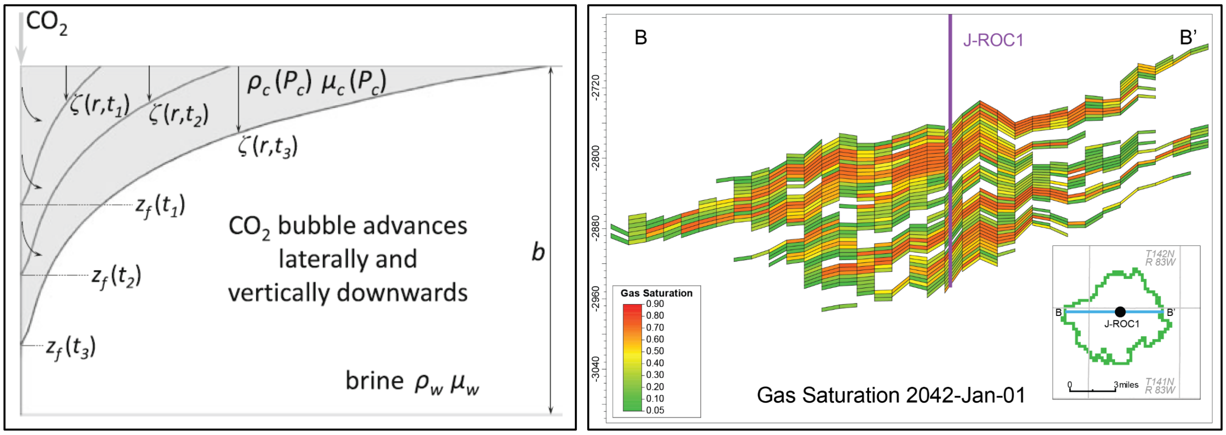

Figure 9. Illustration of CO_2 injection into a deep saline aquifer showing how CO_2 plume thickness at the injection well progressively increases with time as CO_2 is injected (left) (Vilarrasa and others, 2013) and simulated CO_2 plume boundary and cross section at the end of injection displayed east to west through the J-ROC 1 well (right) (source: Minnkota Power Cooperative, Inc., Milton R. Young Station targeting the Broom Creek Formation in Oliver County, North Dakota, Case No. 29029, Order No. 31583 – approved January 2022).

Determine Buoyancy Drive

Using the estimated formation fluid density for the 100,000-ppm scenario (1063 kg/m^3), estimated range in CO_2 density for the two different pressure gradients (699–732 kg/m^3), estimated column heights of CO_2 from 9.1 to 82.3 m, and solving for buoyancy drive using Equation 1 results in an estimated range for buoyancy drive (ΔP) from approximately 4.3 psi (near the CO_2 plume fringe) to 43 psi (near the CO_2 injection well). The calculations below illustrate the four different combinations of variable inputs.

$$\Delta P = \left(1{,}063\,\frac{\mathrm{kg}}{\mathrm{m}^3} - 699\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)\ 9.81\,\frac{\mathrm{m}}{\mathrm{s}^2}\ 9.1\ \mathrm{m} = 32{,}582\ \mathrm{Pa} \times\ (1.45 \times 10^{-4}) = 4.7\ \mathrm{psi}$$

$$\Delta P = \left(1{,}063\,\frac{\mathrm{kg}}{\mathrm{m}^3} - 732\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)\ 9.81\,\frac{\mathrm{m}}{\mathrm{s}^2}\ 9.1\ \mathrm{m} = 29{,}643\ \mathrm{Pa} \times\ (1.45 \times 10^{-4}) = 4.3\ \mathrm{psi}$$

$$\Delta P = \left(1{,}063\,\frac{\mathrm{kg}}{\mathrm{m}^3} - 699\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)\,9.81\,\frac{\mathrm{m}}{\mathrm{s}^2}\;82.3\ \mathrm{m} = 295{,}254\ \mathrm{Pa} \times\ (1.45 \times 10^{-4}) = 43\ \mathrm{psi}$$

$$\Delta P = \left(1{,}063\,\frac{\mathrm{kg}}{\mathrm{m}^3} - 732\,\frac{\mathrm{kg}}{\mathrm{m}^3}\right)\,9.81\,\frac{\mathrm{m}}{\mathrm{s}^2}\;82.3\ \mathrm{m} = 266{,}785\ \mathrm{Pa} \times\ (1.45 \times 10^{-4}) = 39\ \mathrm{psi}$$

These estimates provide plausible ranges for buoyancy drive for this specific example, which must then be evaluated in the context of the cap rock capillary entry pressure.

Step 2 – Evaluate Cap Rock Sealing Capacity

Estimate Maximum Column Height of CO_2

Using the capillary entry pressure of the injection zone and cap rock and the formation fluid and CO_2 density, the maximum column height of CO_2 that the cap rock can retain can be estimated from Equation 4 (Smith, 1966; Schowalter, 1979):

$$H = \frac{\mathrm{P}_{dB} - \mathrm{P}_{dR}}{(\rho_w - \rho_{CO2}) \times 0.433} \qquad \text{[Eq. 4]}$$

Where:

H is the maximum vertical CO_2 column above the 100% water level (CO_2–water contact) that can be contained by the cap rock (ft).
P_{dB} is the CO_2–water entry pressure of the cap rock (psi).
P_{dR} is the CO_2–water entry pressure of the injection zone (psi).
ρ_w is the density of the formation fluid at reservoir pressure and temperature conditions (g/cm^3).
ρ_{CO2} is the density of the CO_2 at reservoir pressure and temperature conditions (g/cm^3).
0.433 is a unit conversion factor for freshwater.

For the examples shown in Section 2, the permeable sandstone sample (injection zone) had an estimated capillary entry pressure of 4 psi (P_{dR}) (Figure 3A), the dolomitic sandstone sample (tighter injection zone) had an estimated capillary entry pressure of 200 psi (P_{dR}) (Figure 3B), and the siltstone sample (cap rock) had an estimated capillary entry pressure of 300 psi (P_{dB}) (Figure 3C). Therefore, using the formation fluid and CO_2 density estimates from the preceding example, the maximum column height of CO_2 that the cap rock can retain (H) would range from 1880 to 2067 ft for the permeable sandstone injection zone and 635–698 ft for the dolomitic sandstone injection zone, as illustrated below.

Permeable Sandstone

$$H = \frac{300\ \mathrm{psi} - 4\ \mathrm{psi}}{(1.063\,\frac{\mathrm{g}}{\mathrm{cm}^3} - 0.699\,\frac{\mathrm{g}}{\mathrm{cm}^3}) \times 0.433} = 1880\ \mathrm{ft}$$

$$H = \frac{300\ \mathrm{psi} - 4\ \mathrm{psi}}{(1.063\,\frac{\mathrm{g}}{\mathrm{cm}^3} - 0.722\,\frac{\mathrm{g}}{\mathrm{cm}^3}) \times 0.433} = 2067\ \mathrm{ft}$$

Dolomitic Sandstone

$$H = \frac{300\ \text{psi} - 200\ \text{psi}}{(1.063\ \frac{\text{g}}{\text{cm}^3} - 0.699\ \frac{\text{g}}{\text{cm}^3}) \times 0.433} = 635\ \text{ft}$$

$$H = \frac{300\ \text{psi} - 200\ \text{psi}}{(1.063\ \frac{\text{g}}{\text{cm}^3} - 0.722\ \frac{\text{g}}{\text{cm}^3}) \times 0.433} = 698\ \text{ft}$$

These results illustrate the interplay between the maximum column height of CO_2 that the cap rock can retain (*H*), injection zone and cap rock capillary entry pressures, and formation fluid and CO_2 densities (a function of injection zone pressure, temperature, and salinity). If *H* is greater than the formation thickness, as they are in this example (the formation thickness is 300 ft), then the result provides confidence in the cap rock sealing capacity.

Estimate Cap Rock Sealing Number

Espinoza and Santamarina (2017) defined the "sealing number" as the ratio of the cap rock capillary entry pressure (P_c) to the buoyancy drive at the injection zone–cap rock interface (ΔP) (Equation 5):

$$\text{Cap Rock Sealing Number} = \frac{P_c}{\Delta P} \qquad \text{[Eq. 5]}$$

A ratio of 1 would indicate that the upward force at the injection zone–cap rock interface (ΔP) and the resistance to the upward force by the cap rock capillary entry pressure (P_c) are equal. Therefore, cap rock sealing numbers greater than 1 represent greater cap rock sealing capacity. The cap rock sealing number provides a rapid, screening-level assessment of cap rock sealing capacity as compared to numerical approaches, which require many additional parameters and can be time- and labor-intensive.

Continuing with the previous example where the siltstone cap rock had a capillary entry pressure of 300 psi and using the ΔP from buoyancy drive of 43 psi near the injection well to 4.3 psi near the fringe of the CO_2 plume results in cap rock sealing numbers of 7–70, respectively.

$$\text{Cap Rock Sealing Number} = \frac{300\ \text{psi}}{43\ \text{psi}} = 7 \text{ (near the injection well)}$$

$$\text{Cap Rock Sealing Number} = \frac{300\ \text{psi}}{4.3\ \text{psi}} = 70 \text{ (near the fringe of the } CO_2 \text{ plume)}$$

Therefore, within the region of the CO_2 plume extent in the injection zone, the resistance to the upward buoyancy force (capillary entry pressure) is 7–70 times greater than the upward force, which provides a measure of confidence in the cap rock sealing capability. EPA "recommends that CCS project owners or operators verify that the capillary entry pressure exceeds pressure increases expected from the buoyancy-driven accumulation of CO_2 in the injection zone" (buoyancy drive) (U.S. Environmental Protection Agency, 2013). Therefore, the cap rock sealing number provides a quantitative basis for assessing compliance with EPA recommendations.

As shown for the three cap rock samples from the PCOR Partnership region presented in Table 1, the capillary entry pressures can be significantly greater than 300 psi, as the black shale sample had an estimated capillary entry pressure of 1317 psi—more than four times greater than the example used above. The cap rock sealing numbers using 1317 psi in the numerator would range from 31 to 306—approximately fourfold greater sealing capacity. Conversely, the capillary entry pressures can be less than 300 psi, as the muddy siltstone had an estimated capillary entry pressure of 129 psi. The cap rock sealing numbers using 129 psi in the numerator would range from 3 to 30—still greater than 1 (the EPA threshold criteria) but lower than the 300-psi example.

CONCLUSIONS

Capillary entry pressure provides an indication of the maximum upward CO_2 force that can be held within the injection zone before CO_2 starts to permeate the cap rock. Capillary entry pressure is proportional to the adhesion tension and inversely proportional to the radius of the pore throat radius. Three main laboratory test methods are commonly used for determining capillary entry pressure: i) centrifuge method, ii) semipermeable membrane (porous plate) method, and iii) mercury–air (mercury injection) method. For CCS projects, HPMI is the most common method for measuring capillary entry pressures, especially for geologic materials with small pore sizes like those found in cap rocks.

The workflow presented herein provides a screening-level assessment method for using capillary entry pressure measurements to estimate cap rock sealing capacity for long-term CO_2 storage. The workflow i) uses established equations from peer-reviewed literature and input values for the parameters of those equations (including capillary entry pressure measurements) and ii) evaluates the cap rock sealing capacity–the ability of the cap rock to resist the upward forces from the stored CO_2 (buoyancy drive). Inputs to this workflow include:

- Pressure and temperature of the injection zone.
- Formation fluid density in the injection zone (a function of the formation pressure, temperature, and salinity).
- CO_2 density in the injection zone (a function of the formation pressure and temperature).
- Column height of CO_2 in the injection zone.
- Capillary entry pressure of the injection zone and cap rock (HPMI measurements).

To the extent practicable, each of these inputs should utilize site-specific characterization data and quantify the uncertainty (noise) inherent in each measurement.

There is no absolute capillary entry pressure number that, in and of itself, can be deemed "good" or "bad." Instead, the capillary entry pressure must be evaluated in the context of the predicted upward CO_2 force at the injection zone–cap rock interface. EPA recommends that CCS project owners or operators verify that the capillary entry pressure exceeds pressure increases expected from the buoyancy-driven accumulation of CO_2 in the injection zone (buoyancy drive) (U.S. Environmental Protection Agency, 2013). The cap rock sealing number is defined as the ratio of the cap rock capillary entry pressure to the buoyancy drive at the injection zone–cap rock interface, therefore providing a quantitative basis for assessing compliance with EPA recommendations. A ratio of 1 would indicate that the upward force at the injection zone–cap rock interface and the resistance to the upward force by the cap rock capillary entry pressure are equal. Therefore, cap rock sealing numbers greater than 1 represent greater cap rock sealing capability capacity, while values less than 1 represent less sealing capability.

REFERENCES

Bachu, S., 2003, Screening and ranking of sedimentary basins for sequestration of CO_2 in geological media: Environmental Geology, v. 44, no. 3, p. 277–289. doi:10.1007/s00254-003-0762-9.

Bandilla, D.J., 2016, BrineDen—an Excel Visual Basic for applications function for calculating brine density: Princeton University.

Battistelli, A., Calore, C., and Pruess, K., 1997, The simulator TOUGH2/EWASG for modelling geothermal reservoirs with brines and non-condensible gas: Geothermics, v. 26, no. 4, p. 437–464.

Buckly, S.E., and Leverett, M.C., 1942, Mechanism of fluid displacements in sands: Transactions of the AIME, v. 146, p. 107–116. https://doi.org/10.2118/942107-G.

Burton-Kelly, M.E., Azzolina, N.A., Connors, K.C., Peck, W.D., Nakles, D.V. and Jiang, T., 2021, Risk-based area of review estimation in overpressured reservoirs to support injection well storage facility permit requirements for CO_2 storage projects: Greenhouse Gases Science and Technology, v. 11, p. 887–906. https://doi.org/10.1002/ghg.2098.

Dandekar, A.Y., 2013, Petroleum reservoir rock and fluid properties: Boca Raton: Taylor & Francis Group.

Duan, Z., Moller, N., and Weare, J., 1992, An equation of state for the CH_4-CO_2-H_2O system—I. pure systems from 0 to 1000C and 0 to 8000 bar: Geochimica et Cosmochimica Acta, v. 56, p. 2605–2617.

Espinoza, D.N., and Santamarina, J.C., 2010, Water-CO_2-mineral systems – interfacial tension, contact angle, and diffusion—implications to CO_2 geological storage: Water Resources Research, v. 46, W07537. doi:10.1029/2009WR008634.

Espinoza, D.N., and Santamarina, J.C., 2017, CO_2 breakthrough—caprock sealing efficiency and integrity for carbon geological storage: International Journal of Greenhouse Gas Control, v. 66, p. 218–229. ISSN 1750-5836.

Haas, J.L., 1976, Physical properties of the coexisting phases and thermochemical properties of the H_2O component in boiling NaCl solutions: USGS Bulletin 1421-A, Washington, D.C., p. 73.

International Organization for Standardization, 2017, Carbon dioxide capture, transportation, and geological storage—geological storage: ISO 27914:2017.

McPhee, C., Reed, J., and Zubizarreta, I., 2015, Core analysis—a best practice guide: Elsevier, 852 p. 9780444636577.

National Institute of Standards and Technology, 2022, Thermophysical properties of fluid systems, https://webbook.nist.gov/chemistry/fluid/ (accessed November 2022).

Nordbotten, J.M., Celia, M.A., and Bachu, S., 2005, Injection and storage of CO_2 in deep saline aquifers—analytical solution for CO_2 plume evolution during injection: Transport in Porous Media, v. 58, p. 339–360. https://doi.org/10.1007/s11242-004-0670-9.

Schowalter, T.T., 1979, Mechanics of secondary CO_2 migration and entrapment: American Association of Petroleum Geologists Bulletin, v. 63, no. 5, p. 723–760.

Smith D.A., 1966, Theoretical consideration of sealing and non-sealing faults: American Association of Petroleum Geologists Bulletin, v. 50, no. 2, p. 363–374.

Span, R., and Wagner, W., 1996, A new equation of state for carbon dioxide covering the fluid region from triple point temperature to 1000K at pressures up to 800 MPa: Journal of Physical Chemistry v. 5, no. 6, p. 1509–1596.

U.S. Environmental Protection Agency, 2013, Underground injection control Program Class VI implementation manual for UIC program directors: EPA 816-R-13-004.

Vilarrasa, V., Carrera, J., Bolster, D., and Dentz, M., 2013, Semianalytical solution for CO_2 plume shape and pressure evolution during CO_2 injection in deep saline formations: Transport in Porous Media, v. 97, p. 43–65. https://doi.org/10.1007/s11242-012-0109-7.

Weyer, K.U, 1978, Hydraulic forces in permeable media: Mémoires du B.R.G.M., Orléans, France, v. 91, p. 285–297.