Effects of rock mineralogy and pore structure on stress-dependent permeability of shale samples

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We conducted pulse-decay permeability experiments on Utica and Permian shale samples to investigate the effect of rock mineralogy and pore structure on the transport mechanisms using a non-adsorbing gas (argon). The mineralogy of the shale samples varied from clay rich to calcite rich (i.e. clay poor). Our permeability measurements and scanning electron microscopy images revealed that the permeability of the shale samples whose pores resided in the kerogen positively correlated with organic content. Our results showed that the absolute value of permeability was not affected by the mineral composition of the shale samples. Additionally, our results indicated that clay content played a significant role in the stress-dependent permeability. For clay-rich samples, we observed higher pore throat compressibility, which led to higher permeability reduction at increasing effective stress than with calcite-rich samples. Our findings highlight the importance of considering permeability to be stress dependent to achieve more accurate reservoir simulations especially for clay-rich shale reservoirs.

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1. Introduction

Understanding the transport mechanisms in shale reservoirs is essential for a number of applications including reservoir characterization, field development and production forecasting. Shale reservoirs are complex and heterogeneous geological systems. The mineralogy, total organic carbon (TOC) content and the texture of the organic-rich shales are highly variable.
In this paper, we investigated the lithological controls on the matrix permeability of Utica and Permian shale samples. The mineralogy of the shale samples varied from clay rich to calcite rich. The TOC content ranged between 1.0% and 5.9%. Permeability measurements were conducted using a non-adsorbing gas (argon) at effective stresses ranging between 500 psi (3.45 MPa) and 4000 psi (27.6 MPa). The effects of mineralogy and TOC on the intrinsic permeability and the stress-dependent permeability were studied. Permeability measurements were also conducted using an adsorbing gas (CO₂) to investigate the effect of CO₂ adsorption on permeability. The CO₂ permeability measurements will be discussed in a future publication.

2. Sample descriptions

Permeability experiments were conducted on four intact Utica shale samples and three intact Permian shale samples of varying mineral composition. The samples were collected from two different wells drilled in the Utica and Permian shales. The ternary diagram (figure 1) shows the mineral composition of the tested Utica and Permian shale samples. The plot indicates that the mineral composition of the shale samples varied from clay and quartz rich to calcite rich. The four Utica sample sets contained both horizontally oriented samples and vertically oriented samples. The Permian samples were vertically oriented samples.

Table 1 lists the results of vitrinite reflectance, TOC and X-ray diffraction (XRD) analyses for the Utica samples. The rock analyses were conducted on samples 0.3–0.9 m (1–3 ft) deeper or shallower than the actual received samples. The samples were organic rich (1.7–3.3 wt% TOC). Their thermal maturity ranged between 0.99% and 1.18% R₀. The clay content varied from 11 wt% (sample U4) to 49 wt% (sample U1). Illite was the predominant clay mineral (7–34 wt%). The carbonate content ranged between 12 and 80 wt% with calcite as the predominant carbonate mineral (7–78 wt%).

Table 2 lists the results of vitrinite reflectance, TOC and XRD analyses for the Permian samples. Similar to the Utica samples, the analyses were conducted on samples 0.3–0.9 m (1–3 ft) deeper or shallower than the actual received samples. The Permian samples contained 0.8–5.9 wt% TOC. The clay content varied from 5.5 wt% (sample P2) to 53 wt% (sample P4). The clay types were illite (2.7–21.9 wt%), mixed layer smectite/illite (2.8–19.2 wt%) and chlorite (0–15.3 wt%).
Figure 2. The hydrostatic permeability system inside the thermal isolation chamber. (Online version in colour.)

Table 1. Summary of vitrinite reflectance (% $R_o$), TOC (wt%) and XRD analysis (wt% without TOC) for the Utica samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>$R_o$</th>
<th>TOC</th>
<th>clays</th>
<th>carbonates</th>
<th>quartz</th>
<th>feldspar</th>
<th>pyrite</th>
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<tbody>
<tr>
<td>U1</td>
<td>0.99</td>
<td>2.4</td>
<td>49</td>
<td>12</td>
<td>28</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>U2</td>
<td>1.02</td>
<td>1.7</td>
<td>41</td>
<td>26</td>
<td>26</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>U3</td>
<td>1.07</td>
<td>3.3</td>
<td>20</td>
<td>55</td>
<td>19</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>U4</td>
<td>1.18</td>
<td>2.1</td>
<td>11</td>
<td>80</td>
<td>7</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2. Summary of vitrinite reflectance (% $R_o$), TOC (wt%) and XRD analysis (wt% without TOC) for the Permian samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>$R_o$</th>
<th>TOC</th>
<th>clays</th>
<th>carbonates</th>
<th>quartz</th>
<th>feldspar</th>
<th>pyrite</th>
</tr>
</thead>
<tbody>
<tr>
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<td>5.9</td>
<td>27.0</td>
<td>27.8</td>
<td>35.4</td>
<td>6.5</td>
<td>3.3</td>
</tr>
<tr>
<td>P2</td>
<td>0.89</td>
<td>1.0</td>
<td>5.5</td>
<td>68.8</td>
<td>17.5</td>
<td>7.2</td>
<td>1.0</td>
</tr>
<tr>
<td>P4</td>
<td>—</td>
<td>0.8</td>
<td>53.0</td>
<td>7.9</td>
<td>25.3</td>
<td>11.1</td>
<td>2.7</td>
</tr>
</tbody>
</table>

carbonate content ranged between 7.9 and 68.8 wt%. The carbonate was calcite (3.8–24.2 wt%) and dolomite (2.6–44.6 wt%).

3. Experimental apparatus

Permeability experiments were conducted in a hydrostatic pressure vessel. The hydrostatic permeability system is shown in figure 2. The three main components of the system were the pressure vessel that holds the core, the pore pressure controller and the confining pressure controller. The pressure vessel was a Temco HCH bi-axial hydrostatic core holder. The pore pressure was controlled by a Quizix QX1500 pump, which was connected to the gas cylinder and which includes two independently controlled motor-driven pistons. One piston was connected to the upstream side of the core holder and the other piston was connected to the downstream side. The pump can operate in different operating modes including constant pressure or constant flow rate. The pressures and flow rates were measured by the Quizix system at an accuracy of ±0.01% and ±0.1%, respectively. The confining pressure was controlled using an Isco pump. A Heise DXD pressure transducer was used to measure the confining pressure at an accuracy of ±0.1%.
Figure 3. Pore pressures ($P_p$) and confining pressures ($P_c$) during cycles of permeability measurements with Ar and CO$_2$ for the Utica and Permian samples.

All experiments were conducted at a temperature of 38°C with only ±0.1°C temperature fluctuation over testing periods lasting several months. Temperature stability was achieved by enclosing the hydrostatic permeability system within a thermal isolation chamber and installing a heat control system. The heat control system consisted of a heat generator and a fan. The heat generator turned on and off within the intended temperature window using a feedback algorithm implemented via LabView. The fan was always kept on during the experiment to circulate the air and keep the temperature constant in the thermal isolation chamber.

4. Methodology

Permeability measurements for each sample were conducted at different pore pressures and confining pressures. Figure 3 illustrates the permeability measurement programme with Ar and CO$_2$. The programme contains several loading and unloading cycles. During a single loading and unloading cycle, the pore pressure was maintained constant and the confining pressure was stepwise increased to the maximum effective stress and then stepwise decreased. At each step, a single permeability measurement was conducted using the pressure pulse decay technique.

As shown in figure 3, the sequence of a set of permeability experiments consisted primarily of several Ar cycles followed by a CO$_2$ cycle that was followed by a single Ar cycle. Before introducing a new pore fluid, the system including the sample was under vacuum overnight. Then, the pore fluid was injected at the target pore pressure and the sample was left to saturate for 24 h prior to the Ar cycle or 48 h prior to the CO$_2$ cycle. The purpose of the Ar cycles was to study the Klinkenberg effects and to investigate stress-dependent permeability. The permeability during one of the cyclic loadings with Ar was also used as a reference point to compare with the CO$_2$ permeability obtained from the CO$_2$ cycle. Hence, the purpose of the CO$_2$ cycle was to investigate the effect of CO$_2$ adsorption on permeability. The last Ar cycle was included in the testing programme to investigate permeability recoverability. This paper will focus only on discussing the Ar cycles (pre-CO$_2$).

(a) Pressure pulse decay technique

In the pressure pulse decay technique, a pressure step was introduced in the upstream side, while the pressure response on the downstream side was measured. Pressure transducers in each cylinder of the Quizix pump were used to measure the pressure in the upstream and downstream reservoirs. To generate the upstream pressure step, the equilibrium pore pressure was increased by nearly 10%.
The model by Brace et al. [1] was used to estimate the permeability of the shale samples. First, the natural logarithm of the difference between the upstream and the downstream pressure was plotted as a function of time. The pressure difference follows an exponential decay:

$$\Delta p(t) = \Delta p_0 e^{-\alpha t}, \quad (4.1)$$

where $\Delta p(t)$ is the difference between the upstream pressure and the downstream pressure at time $t$, $\Delta p_0$ is the difference in pressure at time $t = 0$, $t$ is time and $\alpha$ is the decay exponent. Then, the slope of the linear trend between the logarithm of pressure difference and time (i.e. the decay exponent, $\alpha$) was used to compute permeability with the following equation:

$$\alpha = \frac{kA}{\mu \beta L} \left( \frac{1}{V_{\text{up}}} + \frac{1}{V_{\text{down}}} \right), \quad (4.2)$$

where $k$ is the sample permeability, $A$ is the sample cross-sectional area, $\mu$ is the gas viscosity at the given temperature and pressure conditions [2], $\beta$ is the gas compressibility [3], $L$ is the length of the sample, $V_{\text{up}}$ is the upstream volume and $V_{\text{down}}$ is the downstream volume. An example of an upstream pressure pulse generated to measure the permeability of Utica sample U1 at 300 psi (2 MPa) pore pressure and 800 psi (5.5 MPa) confining pressure is shown in figure 4. The generated upstream pressure pulse was maintained constant, creating an infinite upstream reservoir volume. Therefore, equation (4.2) can be reduced to

$$\alpha = \frac{kA}{\mu \beta LV_{\text{down}}}. \quad (4.3)$$

(b) Klinkenberg analysis

Klinkenberg [4] discovered that slip flow occurs when the pore diameter of a porous medium approaches the mean free path of the flowing gas molecules. This results in an increase in the frequency of collisions between the gas molecules and the rock walls, leading to an additional
flux at the wall surface that enhances the flow rate. This phenomenon is called the Klinkenberg effect and it is expressed as follows:

\[ k_{\text{gas}} = k_\infty \left(1 + \frac{b_{\text{slip}}}{p}\right), \]  

where \( k_{\text{gas}} \) is the gas or apparent permeability, \( k_\infty \) is the intrinsic or Klinkenberg-corrected permeability, \( b_{\text{slip}} \) is the Klinkenberg slip factor and \( p \) is the pore pressure during the permeability experiment.

A plot of measured gas permeability as a function of reciprocal mean pore pressure should reveal a straight line that can be analysed to calculate the Klinkenberg-corrected permeability and the Klinkenberg slip factor. The Klinkenberg-corrected permeability is calculated from the \( y \)-intercept and the Klinkenberg slip factor is calculated from the slope of the straight line. The following expression by Klinkenberg [4] relates the Klinkenberg slip factor \( (b_{\text{slip}}) \) to the mean free path \( (\lambda) \) and the pore radius \( (r) \):

\[ b_{\text{slip}} = \frac{4pc\lambda}{r}, \]  

where \( c \) is a proportionality factor \((c = 1)\). The mean free path is defined as the average distance a molecule travels before it collides with another molecule. Mathematically, it is defined as [5]

\[ \lambda = \frac{k_B T}{\sqrt{2\pi \delta^2 p}}, \]  

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \delta \) is the collision diameter of the gas molecule and \( p \) is the pressure. In the simplest version of the kinetic theory of gases, molecules that make binary collisions only can be treated as hard spheres of diameter \( d \). In this case, \( \delta \) in the mean free path formula (equation (4.6)) can just be replaced with the molecular diameter \( d \). Equation (4.6) can then be rewritten as

\[ \lambda = \frac{k_B T}{\sqrt{2\pi d^2 p}}. \]  

By combining equations (4.5) and (4.7), a mean pore throat radius can be calculated from the Klinkenberg plot using the following expression:

\[ r = \frac{4}{b_{\text{slip}}} \frac{k_B T}{\sqrt{2\pi d^2}}. \]  

(c) Stress-dependent permeability

Porous media deform under stress, causing the permeability to change. Thus, permeability is a function of effective stress. Many researchers have reported that shale permeability decreases with increasing effective stress [6–10]. In this work, the stress-dependent permeability was determined by measuring the permeability of the samples over a range of effective stresses. The stress dependence of permeability can be described according to the following exponential function [10–13]:

\[ k_\infty = k_0 e^{-c_m \sigma_{\text{eff}}}, \]  

where \( k_\infty \) is the Klinkenberg-corrected permeability, \( k_0 \) is the permeability at zero effective stress, \( c_m \) is the slope of the line and is a measure of pore throat compressibility, and \( \sigma_{\text{eff}} \) is the effective stress. \( \sigma_{\text{eff}} \) is the simple effective stress and it is defined as the difference between the confining pressure and the pore pressure,

\[ \sigma_{\text{eff}} = pc - p_p. \]  

5. Results and data processing

As previously shown on the testing programme (figure 3), the characterization of the samples consisted of a number of cyclic loadings of permeability measurements. Each step in the loading
Figure 5. Apparent argon permeability as a function of effective stress for the bedding-parallel Utica samples: (a) U1, (b) U2, (c) U3 and (d) U4. The key indicates the pore pressures at which the permeability measurements were conducted. Note that the range of the x-axis and y-axis changes from one plot to another.

Figure 6. Apparent argon permeability as a function of effective stress for the bedding-perpendicular Permian samples: (a) P2 and (b) P4. The key indicates the pore pressures at which the permeability measurements were conducted. Note that the range of the y-axis is different in both plots.

phase and unloading phase represents a single permeability measurement by the pressure pulse decay technique. Figure 5 shows the apparent Ar permeability (bedding parallel) as a function of the effective stress for the Utica samples U1, U2, U3 and U4. The plots indicate that, as the effective stress increases, the apparent permeability decreases due to pore compaction. Additionally, the plots indicate that, as the pore pressure decreases, the apparent permeability increases due to slippage effects. The highest apparent Ar permeability ($2.05 \mu d$) was observed for U3 at 200 psi (1.38 MPa) pore pressure and 500 psi (3.45 MPa) effective stress. The lowest apparent Ar permeability ($0.036 \mu d$) was observed for sample U2 at 900 psi (6.21 MPa) pore pressure and 2000 psi (20.7 MPa) effective stress.

Argon permeability measurements were conducted on samples P2 and P4 from the Permian samples. The permeability measurements for sample P1 were aborted because its permeability was too low, causing the testing programme duration to be too long (weeks). Figure 6 shows the apparent Ar permeability (bedding perpendicular) as a function of the effective stress for
Permian samples P2 and P4. The apparent permeability behaviour was similar to the apparent permeability behaviour observed for the Utica samples. Pore compaction at higher effective stresses caused the apparent permeability to decrease and slip effects at low pore pressures caused the apparent permeability to increase. In addition, the apparent permeability of sample P2 was higher than the apparent permeability of sample P4. The highest apparent permeabilities measured for samples P2 and P4 at 200 psi (1.38 MPa) pore pressure and 500 psi (3.45 MPa) effective stress were 6.24 $\mu d$ and 1.34 $\mu d$, respectively.

Klinkenberg analyses were carried out for the Utica and Permian samples. The apparent Ar permeability was plotted as a function of the reciprocal mean pore pressure for the six samples at different effective stresses (figure 7). Slippage effects are clearly observed for all the samples. As the pore pressure decreases ($1/p$ increases on the Klinkenberg plot), the apparent permeability increases. The plotted data were fitted linearly with a straight line. The slope and $y$-intercept of the best-fit straight lines are shown in table 3. From equation (4.4), the slope and $y$-intercept can be defined as

\[
slope = k_\infty b_{\text{slip}},
\]

and

\[
y_{\text{intercept}} = k_\infty.
\]
Table 3. Data obtained from the Klinkenberg analysis plots for all samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>$\sigma_{\text{eff}}$ (psi)</th>
<th>slope (µ$d$ psi)</th>
<th>$y$-intercept (µ$d$)</th>
<th>$b_{\text{slip}}$ (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1</td>
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<td>118.4</td>
<td>0.706</td>
<td>167.7</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>75.1</td>
<td>0.497</td>
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<tr>
<td></td>
<td>1500</td>
<td>61.6</td>
<td>0.306</td>
<td>201.3</td>
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<td></td>
<td>2000</td>
<td>54.2</td>
<td>0.183</td>
<td>296.2</td>
</tr>
<tr>
<td>U2</td>
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<td></td>
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6. Discussion

Two parameters were obtained from the Klinkenberg plots: the Klinkenberg slip factor ($b_{\text{slip}}$) and the Klinkenberg-corrected permeability ($k_{\infty}$). The Klinkenberg slip factor ($b_{\text{slip}}$) and the Klinkenberg-corrected permeability ($k_{\infty}$) were estimated using equations (5.1) and (5.2), respectively. The Klinkenberg parameters for the Utica and Permian samples are tabulated in Table 3. The Klinkenberg parameters were used to investigate the effect of shale mineralogy on permeability, to characterize the pores of the shale samples and to evaluate the stress-dependent permeability. Additionally, scanning electron microscopy (SEM) was employed to aid in the pore structure characterization.
Figure 8. Klinkenberg-corrected permeability as a function of effective stress for the Utica (a) and Permian (b) samples.

(a) Effect of shale mineralogy on matrix permeability

The Klinkenberg-corrected permeability values obtained from the y-intercept of the Klinkenberg plots are plotted against effective stress in figure 8. The results indicate that the Klinkenberg-corrected permeability of the Utica and Permian samples varied. At 500 psi (3.45 MPa) effective stress, sample U3 was the most permeable Utica sample ($k_\infty = 0.937 \mu d$) and sample U2 was the least permeable ($k_\infty = 0.107 \mu d$). Sample P2 was the most permeable Permian sample ($k_\infty = 4.679 \mu d$) and sample P1 was the least permeable sample ($k_\infty = 0.0029 \mu d$). Sample P1 is not plotted in figure 8b because only one data point of Klinkenberg-corrected permeability was obtained for this sample (at 500 psi (3.45 MPa) effective stress). Figure 8 also shows that, as the effective stress increases, the permeability of the shale samples decreases. This clearly indicates that rock deformation/compaction at higher effective stresses impacts permeability. Further discussions about the stress-dependent permeability will be presented later.

Figure 9a,b shows the Klinkenberg-corrected permeability at 500 psi (3.45 MPa) effective stress as a function of TOC for the Utica and Permian samples. Figure 9a shows that there is a positive correlation between TOC and permeability. However, this relationship between TOC and permeability was not observed in the measurements of the Permian samples. Although sample P1 had the highest TOC (5.9 wt%), it showed the lowest permeability. Previous studies by Loucks et al. [14] and Sone & Zoback [15] have shown that pore volume resides in the solid organics. Therefore, samples with higher TOC are expected to have higher porosity, which may lead to
higher permeability. However, as observed with the Permian samples, the higher permeability with higher TOC is not always guaranteed because permeability is also a function of how well the pores in the kerogen are connected along the rock samples.

Figure 9c,d shows the Klinkenberg-corrected permeability at 500 psi (3.45 MPa) effective stress as a function of clay content for the Utica and Permian samples. Based on both plots, there is no clear relationship between clay content or mineralogy and permeability. Therefore, shale mineral composition did not have an impact on the magnitude of the Klinkenberg-corrected permeability of the studied Utica and Permian samples.

(b) Pore shape

Figures 10 and 11 show SEM images from the Utica and Permian shale samples, respectively. Studying the SEM images suggests that the dominant conduits to fluid flow in the Utica samples are pores within the kerogen. Pores were also observed within the clay material but they resided mainly in the kerogen. This observation explains the positive correlation between the Klinkenberg-corrected permeability and TOC shown on figure 9a. In the Permian samples, the SEM images indicate that the dominant conduits to flow are interconnected pores between the grain particles. In both samples, the size of the identified pores from the images was between 100 and 200 nm at ambient conditions.

(c) Pore size

Equation (4.8) was applied to estimate the mean pore radius of a porous medium assuming the porous medium contains a number of capillary tubes. The equation was applied to estimate the mean pore radius for both sample sets at different effective stresses. The Ar molecule diameter (d) used in the calculation was 0.358 nm. Figure 12 plots the mean pore diameter for the Permian samples as a function of effective stress. Pore compaction at increasing effective stress caused the mean pore diameter to decrease, as observed in the plot. Overall, the mean pore size of the Permian samples was of the order of tens of nanometres.
Figure 10. SEM images obtained from the Utica shale samples. As seen on the images, the pores are mainly developed within the kerogen with some pores found within the clay.

The plot also suggests that the reduction in the mean pore diameter varied between the two Permian samples. At 3000 psi (20 MPa) effective stress, the mean pore diameter of sample P2 decreased by approximately 25%, whereas the mean pore diameter of sample P4 decreased by approximately 75%. Compared with sample P2, sample P4 contained more clay content (53 wt%). Sone & Zoback [16] investigated the mechanical properties of various shale gas reservoir rocks and observed that the creep deformation in samples with higher clay content was generally more pronounced. Therefore, higher creep deformation for sample P4 caused the pore to further compact, which in turn led to a significant reduction in the mean pore diameter.

Figure 13 plots the mean pore diameter for the Utica samples as a function of effective stress. As observed in the plot, the Utica samples behaved similarly to the Permian samples. As the effective stress increased, the mean pore diameter decreased. The mean pore diameter was also of the order of tens of nanometres. However, the magnitude of the pore size reduction with increasing effective stress for the four samples was comparable, even though their mineral composition (i.e. clay content) varied significantly. This could be attributed to the orientation of the samples. Unlike the Permian samples, the Utica samples were oriented parallel to bedding (horizontal). Therefore, the confining pressure was acting in the bedding-perpendicular direction. As pointed out by Sone & Zoback [16], in addition to mineral composition, the direction of loading with respect to the bedding plane strongly affects creep deformation. In the Utica samples, deformation due to bedding-perpendicular loading may have masked the deformation of the soft components of the shales (clay and kerogen) because it was greater than the deformation of the soft components. This led to rather similar pore compaction among the four samples.
Figure 11. SEM images obtained from the Permian shale samples. As seen on the images, the dominant conduits to flow are mainly interconnected pores between the grain particles.

Figure 12. Mean pore diameter as a function of effective stress for the Permian samples.

Figure 14 shows the Klinkenberg-corrected permeability as a function of the mean pore radius for the Utica and Permian samples. The plot indicates that there is a log-linear relationship between the mean pore radius and the permeability for the studied samples. This is observed in the vertically oriented samples (Permian) and horizontally oriented samples (Utica). This
relationship clearly illustrates the impact of increasing effective stress on the porous media. As the effective stress increases, the porous medium deforms, causing the pores to narrow (figures 12 and 13). As a direct consequence, the permeability of the porous media decreases. Assuming a porous medium of a bundle of capillary tubes, a relationship between pore size and permeability was derived by applying Darcy’s and Poiseuille’s Laws as follows [17,18]:

\[ k_\infty = \phi \frac{r^2}{8\tau^2}, \]  

where \( \phi \) is porosity and \( \tau \) is tortuosity. Equation (6.1) indicates that a log–log plot of permeability as a function of pore radius should have a slope of 2. At \( r = 1 \) nm, the \( y \)-intercept is:

\[ y_{\text{intercept}} = \frac{\phi}{8\tau^2}. \]  

A guiding line with a slope of 2 is shown in figure 14 for illustration purposes and it is not a best-fit line for the data. The data points for each sample are expected to show a different \( y \)-intercept (at \( r = 1 \) nm) because, as indicated by equation (6.2), the \( y \)-intercept is a function of porosity (\( \phi \)) and tortuosity (\( \tau \)) and those parameters are sample dependent. However, figure 14 shows that the trend for each sample is nearly parallel to the guiding line, suggesting that the porous medium resembles a tortuous capillary tube. Obviously, the mean pore throat diameter calculation was dependent on the Klinkenberg-corrected permeability (equations (4.8) and (5.1)).

**Figure 13.** Mean pore diameter as a function of effective stress for the Utica samples.

**Figure 14.** A log–log plot of the Klinkenberg-corrected permeability as a function of the mean pore radius.
**Figure 15.** Semilog plot of the Klinkenberg-corrected permeability as a function of effective stress for the Utica and Permian samples. The best-fit lines are shown.

**Table 4.** Data obtained from the best-fit lines of the stress-dependent permeability analysis.

<table>
<thead>
<tr>
<th>sample</th>
<th>( k_0 ) (( \mu \text{d} ))</th>
<th>( c_m ) (( -1 \text{ MPa}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1</td>
<td>1.1655</td>
<td>0.132</td>
</tr>
<tr>
<td>U2</td>
<td>0.1298</td>
<td>0.061</td>
</tr>
<tr>
<td>U3</td>
<td>1.0604</td>
<td>0.060</td>
</tr>
<tr>
<td>U4</td>
<td>0.1424</td>
<td>0.049</td>
</tr>
<tr>
<td>P2</td>
<td>4.578</td>
<td>0.006</td>
</tr>
<tr>
<td>P4</td>
<td>1.030</td>
<td>0.078</td>
</tr>
</tbody>
</table>

However, independent mean pore throat size estimates through the SEM at ambient conditions (figures 10 and 11) were equivalent to the pore throat size estimates of the Klinkenberg analysis (100–200 nm in diameter). Therefore, the observations of figure 14 are plausible and confirm that the flow conduits for the shale samples are circular.

**(d) Stress-dependent permeability**

The Utica and Permian samples showed a nonlinear reduction in Klinkenberg-corrected permeability with increasing effective stress (figure 8). The exponential relationship (equation (4.9)) describes well the stress-dependent permeability. **Figure 15** shows the Klinkenberg-corrected permeability of the Utica and Permian samples as a function of effective stress on a semilog plot. The permeability data for each well were fitted with an exponential line. The slope of the line (\( c_m \)) represents the pore throat compressibility and the \( y \)-intercept (\( k_0 \)) represents the permeability at zero effective stress. Data from the best-fit lines are tabulated in table 4.

**Figure 16** plots the slope of the line (\( c_m \)) as a function of clay content. The plot indicates that there is a positive relationship between clay content and the sample’s sensitivity to effective stress. As the clay content increases, the sensitivity of the shale’s permeability to variation in effective stress increases. Among the six samples, the highest sensitivity to effective stress (0.132 MPa\(^{-1}\)) was observed for sample U1, which contained 49 wt% clay. The lowest sensitivity to effective stress (0.006 MPa\(^{-1}\)) was observed for sample P2 (5.5 wt% clay), even though sample P2 showed the highest permeability measurement. According to Chalmers et al. [12], one is more likely to observe greater sensitivity to changes in effective stress in samples that have higher permeability. This, however, was not observed here, indicating that stress-dependent permeability was greatly influenced by rock mineralogy, particularly clay content.
7. Conclusion

Laboratory experiments were conducted to study the effect of shale mineralogy on permeability. Permeability measurements indicated that shale mineralogy did not show a clear effect on the magnitude of permeability. Relatively high permeabilities were observed for both clay-rich and calcite-rich samples. Permeability measurements also showed that there was a positive correlation between permeability and TOC in the Utica samples. SEM images obtained for Utica samples confirmed that their pores resided mainly in the kerogen. SEM images obtained for the Permian samples showed that their flow conduits were interconnected pores between grain particles. The mean pore throat diameters for the Utica and Permian samples were of the order of tens of nanometres, as determined by the Klinkenberg analysis and SEM imaging. The plot of Klinkenberg-corrected permeability as a function of mean pore radius confirmed that the flow conduits were circular and resemble tortuous capillary tubes. Stress-dependent permeability analysis showed that the sensitivity of shale permeability to variations in effective stress was influenced mainly by rock mineralogy. This means that, as clay content increases, shale permeability becomes more sensitive to effective stress. In shale reservoirs, effective stress measured as the difference between overburden stress and pore pressure increases as hydrocarbons are being recovered. This leads to the permeability of the near-wellbore region being lower than the permeability of the outer region, introducing a positive skin factor. Therefore, to achieve more accurate reservoir simulations and production forecasting, stress-dependent permeability should be considered especially for clay-rich shale reservoirs.

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Competing interests. The authors declare that they have no competing interests.

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