Impact of heat of sorption on thermal enhanced recovery of sorbed gas from gas shale reservoirs – An experimental and simulation study

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The importance of heat of sorption in the thermal enhanced recovery of gas shale reservoirs is not well understood in the reservoir engineering community. Our results indicate that not accounting for the heat of sorption significantly over-estimated the potential for thermal enhanced gas recovery under heated conditions by about 13%. However, including the heat of sorption parameter under normal operating (isothermal) conditions did not have any effect on production estimates. This suggests that heat of sorption is a significant parameter, and cannot be ignored whilst assessing the potential for thermal enhanced recovery in gas shales.

The multi-physical reservoir simulation was carried out using a modified equation for heat transfer that accounts for heat of sorption. The Langmuir equation was modified to account for the temperature dependence of sorption. Input parameters for the numerical study - sorption, heat of sorption, porosity, and permeability were experimentally measured in the laboratory using a high-pressure rig. The maximum sorption capacity on shale samples used in this study decreased significantly by 25% when the temperature was increased from 60 to 80 °C.

Using sensitivity analysis, shales with high adsorption capacity and low heat of sorption were found to be good candidates for thermal stimulation to enhance sorbed gas recovery.
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_R$</td>
<td>Fractional gas uptake in the reference cell</td>
</tr>
<tr>
<td>$H_L$</td>
<td>Langmuir Heat of Sorption</td>
</tr>
<tr>
<td>$H_i$</td>
<td>Isosteric Heat of Sorption</td>
</tr>
<tr>
<td>$K_C$</td>
<td>Gas storage capacity ratio</td>
</tr>
<tr>
<td>$P_{L\infty}$</td>
<td>Langmuir Pressure at T=\infty</td>
</tr>
<tr>
<td>$P_L$</td>
<td>Langmuir Pressure</td>
</tr>
<tr>
<td>$P_c$</td>
<td>Charge pressure</td>
</tr>
<tr>
<td>$P_e$</td>
<td>Equilibrium pressure</td>
</tr>
<tr>
<td>$P_i$</td>
<td>Initial pressure</td>
</tr>
<tr>
<td>$Q_h$</td>
<td>Heat input into reservoir</td>
</tr>
<tr>
<td>$Q_{if}$</td>
<td>Gas flow into fracture</td>
</tr>
<tr>
<td>$V_L$</td>
<td>Langmuir Volume</td>
</tr>
<tr>
<td>$V_{bulk}$</td>
<td>Bulk volume of sample</td>
</tr>
<tr>
<td>$V_{grain}$</td>
<td>Grain volume of sample</td>
</tr>
<tr>
<td>$V_r$</td>
<td>Reference cell volume</td>
</tr>
<tr>
<td>$V_s$</td>
<td>Sample cell volume</td>
</tr>
<tr>
<td>$V_{sp}$</td>
<td>Specific volume of sample</td>
</tr>
<tr>
<td>$a_1$</td>
<td>Fitting Constant for Langmuir Volume</td>
</tr>
<tr>
<td>$a_2$</td>
<td>Fitting Constant for Langmuir Volume</td>
</tr>
<tr>
<td>$c_g$</td>
<td>Isothermal compressibility</td>
</tr>
<tr>
<td>$q_a$</td>
<td>Absolute amount adsorbed</td>
</tr>
</tbody>
</table>
Natural gas has often been touted as a more sustainable fuel to provide peak load power, emitting nearly 45% less carbon dioxide as coal [1]. However, gas shale fields are typically characterized by a sharp production decline curve, thereby requiring continual hydraulic fracturing treatments to maintain reservoir producibility [2]. This has piqued the research community’s interest in thermal enhanced gas recovery technologies [3–5]. Since physisorption in gas shales is spontaneous, the change in free energy associated with the process is negative (ΔG < 0). Also, physisorption results in gas molecules being stationary in shale pores, resulting in a decrease in entropy (ΔS < 0). Since ΔH = ΔG + T * ΔS, ΔH < 0. Physisorption
is always an exothermic process [6]. Indeed, the temperature effects of sorption have been widely
characterized in the literature. The maximum sorption capacity and the adsorption affinity of
methane in a gas shale are usually a strong functions of temperature [7]. The various physico-
chemical characteristics that affect temperature dependence of sorption have been thoroughly
investigated in the literature [8].

Another key parameter that could be expected to influence the potential for thermal enhanced
recovery is the heat of sorption. This is widely characterized using the isosteric heat of sorption,
the standard enthalpy of adsorption at fixed surface coverage [9,10], and is calculated through
the application of Clausius-Clapeyron equation to the measured sorption isotherm equations
[6,11].

Thermal enhanced recovery has also been investigated by the reservoir engineering community.
In estimating production from a shale reservoir under normal operating conditions, Yu [12]
demonstrated that it was important to include an additional forcing function to the mass transfer
continuity equation in order to account for the contribution to the total gas stored due to sorption.
This model is widely used in the literature to model gas flow in shales under isothermal
conditions [12–16]. The potential for thermal enhanced recovery to displace sorbed gas from
shale reservoirs has been investigated in some detail [4,15]. Teng investigated the effects of
temperature on thermal expansion, thermal fracturing, and thermal volatization in coals in
addition to the temperature dependence of sorption in assessing Thermal Enhanced Recovery
[3]. Liu considered the effect of Microwave Heating technologies on the potential for Thermal
Enhanced Recovery [17]. Wang assessed the potential for electrical heating to release sorbed gas
from shales [18]. But unfortunately, none of the previous simulation studies assessing Thermal
Enhanced Recovery have considered sorption as a multi-physical phenomenon with both heat
and mass transfer effects. The role played by heat of sorption in the reservoir simulations remains
unclear so far. A thorough investigation on the heat transfer effects of sorption on the potential for thermal enhanced recovery would be of interest to the research community.

Importance of heat of sorption is investigated using a series of reservoir simulation studies. A modified version of the governing equation of heat transfer that accounts for the heat of sorption is used for this purpose [19]. Temperature dependence of sorption was modelled using a modified version of the Langmuir equation [7]. Input parameters for the study are obtained from experimental characterization of gas shales in the laboratory. Methane isotherms up to 60 bars on Lothian shale outcrops are measured at 60 and 80 °C using a high-pressure adsorption measurement rig [20]. The corresponding isosteric heats of the isotherms are calculated using the Clausius Clapeyron equation [6]. Shale permeabilities are measured using the late-time technique during helium expansion experiments [21]. Porosities are measured using the water immersion method [22].

2 Methodology and Model Development

2.1 Sample Description and Preparation

Lothian shale outcrops from Straiton were acquired for this study. Samples crushed to 350 - 2000 μm, were treated with water and with Toluene to remove entrenched water and oil. Prior to characterization, samples are outgassed in the rig at about ≈ 150 Torr and 80 °C.

2.2 Manometric Adsorption Measurement Rig

A generic high pressure manometric adsorption measurement rig was designed and fabricated as follows:
A pressure sensor with an accuracy of ±0.001 barg and a temperature sensor with an accuracy of ±0.1 °C are used in the rig. A water bath capable of maintaining set temperatures with an accuracy of ±0.1°C is also included. Data acquisition and analysis for grain volume and sorption measurement were automated using LabVIEW and Python respectively.

2.3 Porosity and Permeability Measurement

The bulk volume of the shales was measured by water immersion of samples that were previously saturated with water for 12 hours [22].

\[
V_{\text{bulk}} = \frac{\text{weight of water displaced}}{\text{density of water}}
\]

In order to measure the grain volume, shales samples are placed in the sample cell and outgassed. The reference cell was filled with Helium to a known pressure, and the valve connecting the reference and sample cell is opened up. Permeability was also calculated from the same experimental data [21].

Grain volume is calculated assuming ideal gas law holds at low pressures:

\[
P_e V_r + P_i (V_e - V_{\text{grain}}) = P_e (V_r + V_e - V_{\text{grain}})
\]
\[ V_{\text{grain}} = V_s - \frac{(P_c - P_e) \times V_r}{P_e - P_i} \]  

Where \( V_{\text{grain}} \) is the grain volume of the shale sample, \( V_s \) is the volume of the sample cell, \( P_c \) is the charge pressure of Helium in the reference cell, \( P_i \) is the initial pressure of Helium in the sample cell, and \( P_e \) is the equilibrium pressure of Helium in the reference and sample cells.

The specific volume of the shales is calculated as:

\[ V_{sp} = \frac{V_{\text{grain}}}{W_s} \]

Where \( V_{sp} \) is the specific volume of the shale sample and \( W_s \) is the weight of the shale sample.

Porosity is calculated as:

\[ \phi = \frac{V_{bulk} - V_{\text{grain}}}{V_{grain}} \]

Cui [21], proposed the following linear equation to find out the permeability of gas shales:

\[ \ln(F_R) = f_0 - s_1 t \]

Where \( F_R \) is calculated from experimental He expansion as [21]:

\[ F_R = 1 - \frac{(K_C + 1)(\rho_{c0} - \rho)}{\rho_{c0} - \rho_0} \]

\( f_0 \) is the intercept, \( s_1 \) is the slope, and \( t \) is the time in seconds.

\( K_C \) is the ratio of the initial gas stored in the void volume of the reference and sample cells, and the pore volume of the gas shale particles [21]:

\[ K_C = \frac{\rho_b V_C}{M \phi} \]

\( \rho_{c0} \) is the average initial gas density in the reference and sample cells [21]:

\[ \rho_{c0} = \frac{\rho_0 V_r + \rho_0 (V_s - V_b)}{V_r + V_s - V_b} \]
Where $\rho_{r0}$ is the average initial density in the reference cell, and $\rho_0$ is the average initial density in the sample cell.

Permeability is calculated from the slope of Equation as [21]:

$$k = \frac{R_a^2 \phi \mu c_g s_1}{\alpha_1^2}$$

(10)

Where, $\alpha_1$ is the first solution to the equation [21],

$$\tan \alpha = \frac{3\alpha}{3 + K_c \alpha^2}$$

(11)

2.4 Adsorption Measurement

Outgassing was performed in situ, as described in the previous section, and the rig is evacuated to $\approx 150 \text{Torr}$ at the experimental temperature. Residual Helium present in the rig after outgassing is measured as:

$$n_{is}(He) = EOS(P, V_v, T)$$

(12)

Where EOS is the chosen Equation of State used to calculate the number of moles, $P$ is the rig pressure, $V_v$ is the sample cell void volume, and $T$ is the rig temperature. In this study, the Peng-Robinson Equation of State is chosen to calculate the amount adsorbed. Sample cell void volume is calculated as:

$$V_v = V_r + V_s - V_{grain}$$

(13)

A known amount of methane is injected into the reference cell. Once a stable temperature and pressure profile are achieved, the valve connecting reference and sample cells is opened. Total injected # moles is calculated as:

$$n_{ir} = EOS(P_{r,f}, V_r, T) - EOS(P_{r,i}, V_r, T)$$

(14)

Where, $n_{ir}$ is the number of moles injected into the reference cell, $P_{r,f}$ is the final pressure of the reference cell, and $P_{r,i}$ is initial pressure of the reference cell.
# moles present in the rig at any given instance is calculated as:

\[ n_c = EOS(P_s, V_p, T_s) \]  \hspace{1cm} (15)

Excess adsorbed # moles for the nth pressure step is calculated as:

\[ q_e = n_{ir}(1) + n_{ir}(2) + \cdots + n_{ir}(n) + n_{is} - n_c \]  \hspace{1cm} (16)

Where, \( n_{ir}(n) \) is the number of moles injected at nth pressure step.

In order to determine the equilibrium amount sorbed, a rolling regression between excess sorbed and time was performed to find out the rate of sorption. Equilibrium was assumed when the rate of sorption per hour was an order of magnitude lower than the amount adsorbed in a given pressure step (\( \approx 0.001 \frac{mol}{kg \cdot hr} \)). It was noted that approximately 5 hours were required to reach equilibrium in a given pressure step.

Experimentally observed excess sorption values are corrected to absolute sorption values through the following equation [23]:

\[ q_a = \frac{q_e}{1 - \frac{\rho_g}{\rho_{ads}}} \]  \hspace{1cm} (17)

Where, \( \rho_g \) is the gas phase molar density, and \( \rho_{ads} \) is the adsorbed phase molar density, assumed to be equal to the liquid density of the adsorptive (0.4224 g/cm³).

In this study, the desorption isotherms are considered over adsorption isotherms as these govern the gas production mechanisms from shale reservoirs.

### 2.5 Adsorption Isotherms
It is now well recognized that sorption in gas shales is primarily driven by micro-pore filling [24], which is theoretically modelled using the potential theory [25]. Other models such as the Freundlich, Sips, UNILAN, and Toth have also been considered in the literature to model Type I isotherms, but the Langmuir model is the most commonly used by far given its simplicity [26]:

\[ q_a = \frac{V_L P}{P_L + P} \]  

where \( q_a \) is the amount adsorbed, \( V_L \) is the Langmuir volume, and \( P_L \) is the Langmuir pressure given as the inverse of the Langmuir affinity constant \( P_L = \frac{1}{b} \).

2.5.1 Pressure Dependence of Sorption

The first derivative of the Langmuir isotherm with respect to pressure at a given temperature is given as:

\( \left( \frac{\partial q_a}{\partial P} \right)_T = \frac{V_L P_L}{(P + P_L)^2} \)  

2.6 Isosteric heat of sorption

The Clausius-Clapeyron equation was used to model the isosteric heats of sorption [6]:

\[ H_i = -RT^2 \left( \frac{\partial \ln P}{\partial T} \right)_{q_a} \]  

Since, only 2 isotherms, measured at 60 °C and 80 °C are used in this study, isosteric heat was calculated using the following formula:

\[ \ln \left( \frac{P_1}{P_2} \right) = -\frac{H_i}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

2.6.1 Temperature Dependence of Sorption
Although it is possible to account for the temperature dependence of sorption using isosteric heats [11], it is more computationally efficient to account for the temperature dependence of sorption based on the temperature dependence of isotherm parameters. The temperature dependence of Langmuir pressure in equation (18) is represented as follows [6]:

\[ P_L = P_{L\infty} \exp \left( -\frac{H_L}{RT} \right) \]

(22)

Where \( P_{L\infty} \) is the Langmuir pressure at infinite temperature, \( H_L \) is the Langmuir heat of sorption.

Theoretically, the Langmuir volume is independent of temperature. However, this is not the case for most practical applications [11,27]. Some studies have considered using an empirical method to calculate Langmuir volume at different temperatures [7]:

\[ V_L = \left( a_1 + \frac{a_2}{T} \right) \]

(23)

Where \( a_1 \) and \( a_2 \) are fitting constants. Temperature dependence of other isotherms could be found in the literature [6].

Equation (18) could then be modified to give the temperature-dependent form of the Langmuir equation as:

\[ q_a = \frac{\left( a_1 + \frac{a_2}{T} \right) P}{P_{L\infty} \exp \left( -\frac{H_L}{RT} \right) + P} \]

(24)

The first derivative of amount adsorbed with respect to temperature for a Langmuir isotherm could then be calculated as:

\[ \frac{\partial q_a}{\partial T} = -\frac{a_2 P}{T^2(P_L + P)} - \frac{P P_L V_L H_L}{RT^2(P_L + P)^2} \]

(25)

The derivation of Equation (25) can be found in the Appendix.

2.7 Reservoir Model
2.7.1 Mass Transfer Governing Equation

The governing equation for mass transfer in the shale matrix in the presence of sorption is given as:

\[
\rho_s \frac{\partial q_a}{\partial t} + \frac{\partial}{\partial x} \left( \phi \rho_g \frac{\partial q_a}{\partial x} \right) + \frac{1}{\gamma_g} \left( \frac{\partial q_a}{\partial T} \right)_p \frac{\partial T}{\partial t} + \gamma_g \frac{\partial}{\partial T} \left( \frac{\partial q_a}{\partial T} \right)_P \frac{\partial P}{\partial T} + \nabla \cdot \left( \frac{k_{g,k}}{\mu} \nabla P \right) = -Q_{if} \tag{26}
\]

Where, \( \phi \) is the porosity, \( c_g \) is the compressibility factor, \( \alpha_g \) is the coefficient of thermal expansion, \( \rho_g \) is the gas molar density, \( \rho_s \) is the shale density, \( q_a \) is the amount adsorbed, \( \gamma_g = c_g/\alpha_g \), \( k \) is permeability, \( \mu \) is viscosity, \( Q_{if} \) is gas flow into the fracture.

It is noted that Equation (26) is analogous those used to model diffusion in other thermal enhanced recovery studies [4] but represented in terms of pressure and temperature instead of concentration and velocity. The derivation of Equation (26) is given in the Appendix.

2.7.2 Heat Transfer Governing Equation

The governing equation for heat transfer in the shale matrix in the presence of sorption is given as:

\[
\frac{\partial T}{\partial t} = \left( \phi \rho_g C_p \right) \frac{\partial q_a}{\partial T} + \frac{1}{\gamma_g} \left( \frac{\partial q_a}{\partial T} \right)_p \frac{\partial T}{\partial t} + \nabla \cdot \left( \phi \lambda_g \frac{\partial T}{\partial x} \right) + \nabla \cdot \left( \frac{k_m}{\mu} \nabla T \right) + \frac{\rho_g C_p}{\mu} \frac{\partial q_a}{\partial T} \frac{\partial P}{\partial T} \tag{27}
\]
Where $H_i$ is the isosteric heat of sorption, $C_p$ is specific heat capacity, $\lambda$ is heat conductivity, $Q_h$ is heat input into the reservoir.

Equation (27) has been used previously in the literature to model heat transfer in the presence of sorption [19]. However previous studies on thermal enhanced gas recovery have ignored the effect of energy accumulation from adsorbed gas ($H_i$) [4,15].

\[
\begin{align*}
\left[ \phi \rho_g MW C_{pg} + (1 - \phi) \rho_s C_{ps} \right] \frac{\partial T}{\partial t} \\
- \nabla \cdot \left( \phi \lambda_g + (1 - \phi) \lambda_s \right) \nabla T \\
+ \rho_g MW C_{pg} \left( \frac{k_m vP}{\mu} \right) \cdot \nabla T \\
= Q_h
\end{align*}
\]

The Partial Differential Equations and model mass and heat transfer in the shale matrix in the presence of sorption were solved in COMSOL for further analysis.

### 2.7.3 Model Overview

#### 2.7.3.1 Model Geometry

The following model with fractures perpendicular to the wellbore is usually adopted for academic shale reservoir simulation purposes [12,15]. It is noted that the model is symmetric about the wellbore and also with respect to each fracture. Therefore a smaller subdomain of the reservoir was simulated and flow into a single fracture from the Simulated Reservoir Volume was calculated. The fracture was assumed to be at the same temperature as the wellbore [4]. Boundary conditions were applied as applicable as shown in Figure 2. The boundary along the fracture is maintained at a constant temperature and pressure. Boundaries perpendicular to the wellbore were imposed with a no-flow boundary condition due to symmetry. The boundary along
the wellbore is also imposed with a no-flow boundary condition, assuming that produced gas
flows from the matrix to the fracture, and further on to the well-bore [28]. A no-flow boundary
condition is also imposed on the boundary opposite to the well-bore. The governing equations
and are solved with the above mentioned boundary conditions to find out gas flow into the
fracture.

Figure 2 Shale Reservoir Model 1

Figure 3 Finite Element Meshing of the Simulated Reservoir Volume

2.7.3.2 Summary of Model Parameters

Model parameters along with appropriate references are summarised below:

Table 1 Summary of Model Parameters

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shale porosity</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
<td></td>
</tr>
<tr>
<td>----------------------------------</td>
<td>------------------------</td>
<td></td>
</tr>
<tr>
<td>Shale density</td>
<td>2140 kg/m³</td>
<td></td>
</tr>
<tr>
<td>Shale permeability</td>
<td>4.99 x 10⁻²² m²</td>
<td></td>
</tr>
<tr>
<td>Shale specific heat capacity</td>
<td>1000 J/(kg K)</td>
<td></td>
</tr>
<tr>
<td>Initial reservoir temperature</td>
<td>333.15 K</td>
<td></td>
</tr>
<tr>
<td>Initial reservoir pressure</td>
<td>1 x 10⁷ Pa</td>
<td></td>
</tr>
<tr>
<td>Flowing well pressure</td>
<td>3 x 10⁶ Pa</td>
<td></td>
</tr>
<tr>
<td>Methane viscosity</td>
<td>12.18 x 10⁻⁶ Pa s</td>
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</tr>
<tr>
<td>Methane critical temperature</td>
<td>190.55 K</td>
<td></td>
</tr>
<tr>
<td>Methane critical pressure</td>
<td>4599200 Pa</td>
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<tr>
<td>Fracture width</td>
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<td></td>
</tr>
<tr>
<td>Fracture height</td>
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<td></td>
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<tr>
<td>Reservoir height</td>
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<td></td>
</tr>
<tr>
<td>Fracture spacing</td>
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<td></td>
</tr>
<tr>
<td>Method Employed</td>
<td>Finite Element Method</td>
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</tr>
<tr>
<td>Solver Used</td>
<td>MUMPS</td>
<td></td>
</tr>
<tr>
<td>Time Step</td>
<td>1 day</td>
<td></td>
</tr>
</tbody>
</table>

References for Assumptions: ¹ [29]; ²³⁴ [30]

3 Results

3.1 Experimental Shale Characterization

3.1.1 Methane Isotherm
Absolute desorption isotherm values and their corresponding Langmuir fits for 60 and 80 °C are presented in Figure 4. It can be seen that isotherms are Type I up to 60 bars, with Langmuir isotherms providing a good fit. The Langmuir Volume has decreased by about 25% on increasing the temperature from 60 °C to 80 °C, suggesting that increasing reservoir temperature might assist in enhancing adsorbed gas recovery.

![Figure 4 Methane Desorption Isotherms with Langmuir Fits](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>-0.51 mol/kg</td>
</tr>
<tr>
<td>$a_2$</td>
<td>231.47 mol K/kg</td>
</tr>
<tr>
<td>$P_{L\infty}$</td>
<td>161749.17 Pa</td>
</tr>
<tr>
<td>$H_L$</td>
<td>-5423.99 J/mol</td>
</tr>
</tbody>
</table>
3.1.2 Isosteric Heat of Sorption

The isosteric heats of sorption obtained by solving the Clausius-Clapeyron Equation at a given surface coverage are plotted in Figure 5. An increase in isosteric heats suggests that strong lateral interactions overpower surface heterogeneities of shales in this case [31].

![Graph showing isosteric heats of sorption with surface coverage on the x-axis and isosteric heat of sorption on the y-axis.]

*Figure 5 Isosteric Heats of Sorption at different Loading Capacities*

3.1.3 Shale Porosity and Permeability

The bulk density of the gas shale was calculated using water immersion as 1.93 g/cc; the grain density from He expansion was 2.14 g/cc; the porosity was then calculated as 10%. Permeability was calculated using the late-time method as $4.99 \times 10^{-22}$. These values are within the range reported in the literature of gas shale characterization [32].
3.2 Reservoir Model Comparison

3.2.1 Comparison under Isothermal Conditions

The governing equations were solved for a period of 20 years, under isothermal conditions, at a wellbore temperature of 333.15 K, both accounting for and ignoring the heat of sorption to assess the importance of isosteric heat of sorption ($H_i$) parameter under isothermal conditions. It was noted that the recovery rate after 20 years is only 1.5%; the recovery rate of sorbed gas is only 0.2%. Although it is possible to increase these numbers by continual hydraulic fracturing treatments, enhanced recovery techniques are essential to realize the full potential of gas shale reservoirs.

Figure 6 Reservoir Model Comparison under Isothermal Boundary Conditions
3.2.2 Comparison with Heated Fracture

The governing equations were solved, maintaining the wellbore temperature at 80 °C for a period of 20 years, with and without accounting for the heat of sorption.

![Figure 7 Reservoir Model Comparison under Heated Boundary Conditions](image)

The total recovery rate with thermal enhanced recovery after 20 years was 23.7% and the recovery rate for sorbed gas was 11.8%. These results suggest that thermal enhanced recovery could be used to increase total recovery rates from the shale reservoir.

<table>
<thead>
<tr>
<th>Simulation Case</th>
<th>Molar Density of Reservoir after 20 years (mol/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal (Hi)</td>
<td>Isothermal (no Hi)</td>
</tr>
<tr>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>Flow into Fracture (x10 6 mol)</td>
<td>Time (Months)</td>
</tr>
</tbody>
</table>

Table 2 Comparison of Molar Density of the Reservoir after 20 years of production for different simulation cases
It can be seen from Figure 6 that the isosteric heat of sorption parameter does not have any effect on reservoir simulation under isothermal conditions. This implies that for normal operating conditions, it is not necessary to account for the heat of sorption. However, the heat of sorption is more significant for thermal enhanced recovery applications; not accounting for the heat effects of sorption significantly overpredicts the potential for thermal enhanced recovery after 20 years of production when the wellbore is maintained at 80 °C. Both total gas production and sorbed gas production are significantly overestimated by 15 % and 17 % respectively. It is therefore
important that any study assessing the potential for thermal stimulation to enhance gas recovery from shales account for both the heat and mass transfer effects of sorption.

Table 2 shows the molar density distribution of total and adsorbed gas in the Simulated Reservoir Volume after 20 years of production. Reservoir heating displaces a significant amount of gas that would otherwise not be produced under isothermal conditions. It can also be seen that when isosteric heat is not considered heating has a bigger effect in displacing sorbed gas. This is expected given that $\Delta H > 0$, for the desorption process that governs gas production from shales.

3.3 Sensitivity Analysis

A number of simulations were run for a period of 5 years, in order to assess the sensitivity of different parameters in the reservoir model.

3.3.1 Total Production Sensitivity to Heating Temperature

There seems to be a strong linear relationship between the heating temperature and the gas production, in the range of reservoir operating parameters considered in this study. It can also be seen from Figure 9 that heat injection results in a higher initial production rate, which is central to determining the economic feasibility of a gas shale reservoir [33]. Higher production rates, later in field life, could also potentially allow the operator to delay costly re-fracturing expenses.
Figure 8 Flow into Fracture at Different Heating Temperatures for 5 years of production

Figure 9 Production Rates at Different Temperatures for the first year of production
Recovery rate has increased significantly due to reservoir heating over a period of 20 years. It was also observed that recovery from sorbed gas after 2 years increased dramatically to 23% with reservoir heating from a base case of 11% without reservoir heating. This suggests that thermal stimulation could bring recovery from sorbed gas forward in the field life cycle. The rest of the study will focus on the potential for reservoir heating to displace sorbed gas from the reservoir.

3.3.2 Sorbed Gas Production Sensitivity to Reservoir Model Parameters

As seen in Figures 10 and 11, both sorbed gas production and total recovery rate after 5 years are strongly dependent on heating temperature. Sorbed Gas production increased by a factor of 1.08 x 10^6 moles, and total recovery rate (including free gas) increased by a factor of 0.5%, per degree of wellbore temperature increase. Although it might be possible that this linear relationship may not hold true for other operating conditions not considered in this study, the thermal simulation of the shale reservoir could be reasonably expected to increase sorbed gas recovery. That said, it is clear that heat of sorption needs to be considered when assessing the potential for thermally enhanced recovery production systems for individual shale plays. Ignoring the heat of sorption over predicts potential for thermal enhanced recovery to increase sorbed gas recovery by about 0.2 x 10^6 moles per degree of heating at well bore after 5 years of production.
At a heating temperature of 80 °C, sorbed gas production with thermal enhanced recovery is strongly correlated with Langmuir volume and weakly correlated with Langmuir Pressure. Whilst the range of permeabilities considered in this study did not affect sorbed gas production significantly, the amount of sorbed gas displaced under heating has an inverse relation to the isosteric heat of sorption, as with increasing heat of sorption, more energy is required to
displace the same amount of sorbed methane. It was also noted that shales with lower porosity, which are associated with higher initially sorbed gas in bulk shales, displaced more sorbed gas under reservoir heating. This implies that shales with higher amount sorbed, but lower heat of sorption may be better candidates for thermal stimulation in order to enhance sorbed gas recovery.

The above mentioned trends were in some cases reversed when considering total gas production instead of sorbed gas production after 5 years. Porosity was positively correlated with total gas production as free gas is more readily produced compared to sorbed gas. The correlation coefficient of Langmuir volume against total gas production was weakly correlated; Langmuir pressure and isosteric heat of sorption also exhibited a weak negative correlation.
It was noted that the reservoir permeability did not have a significant effect of thermal stimulation to enhance sorbed gas recovery in this study. That said we emphasize that the range of permeability considered in this study is in the nano-Darcy range (2.5 x 10^{-22} to 7.5 x 10^{-22} m^2). We expect that permeability beyond this range could significantly affect production, but is not considered explicitly in this study.

The results of this section are fairly intuitive given that, with increasing heat of sorption, more heat would need to be injected to displace a given amount of sorbed methane. That said the most significant control on the potential for thermal stimulation remains to be the adsorption capacity of the gas shale.

4 Conclusion
Experimentally measured sorption values are used to assess the potential for thermal simulation to enhance sorbed gas recovery by considering sorption as a multi-physical phenomenon with both mass and heat transfer effects. The governing equation for heat transfer is modified to account for the heat of sorption. The Langmuir equation is modified to account for the temperature dependence of sorption.

Adsorption was strongly controlled by temperature. Also, the heat of sorption increased with increasing sorption. Not accounting for the heat of sorption significantly over-estimated the potential for thermal enhanced recovery in gas shales.

Potential for thermal stimulation was strongly controlled by the adsorption capacity but inversely related to the heat of sorption.

Acknowledgement

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References


Bell IH, et al. Pure and Pseudo-pure Fluid Thermophysical Property Evaluation and the
6.1 Derivation of the Temperature Dependence of Amount Adsorbed Based on the Langmuir Equation

Amount adsorbed is calculated from the Langmuir Equation as follows:

\[ q_a = \frac{V_L P}{P_L + P} \]  \hspace{1cm} (29)

Temperature dependence of Langmuir constants are given as follows:

\[ P_L = P_{L,\infty} \exp \left( -\frac{H_L}{RT} \right) \]  \hspace{1cm} (30)

\[ V_L = \left( a_1 + \frac{a_2}{T} \right) \]  \hspace{1cm} (31)

Substituting Equations (30) and (31) in Equation (18), the temperature dependent form of the Langmuir Equation is given as:
\[ q_a = \frac{(a_1 + \frac{a_2}{T})P}{P_L \infty \exp \left( -\frac{H_L}{RT} \right) + P} \quad (32) \]

Differentiating Equation (32) with respect to T:

\[
\left( \frac{\partial q_a}{\partial T} \right)_P = \frac{\frac{a_2}{T^2} \cdot \left( P_L \infty \exp \left( -\frac{H_L}{RT} \right) + P \right) - \left( \frac{a_2}{T^2} + a_2 \right) \cdot \frac{H_L P_L \infty \exp \left( -\frac{H_L}{RT} \right)}{R T^2}}{(P_L \infty \exp \left( -\frac{H_L}{RT} \right) + P)^2} \quad (33)
\]

\[
\left( \frac{\partial q_a}{\partial T} \right)_P = P \cdot \frac{-\frac{a_2}{T^2} \cdot \left( P_L \infty \exp \left( -\frac{H_L}{RT} \right) + P \right) - \left( \frac{a_2}{T^2} + a_2 \right) \cdot \frac{H_L P_L \infty \exp \left( -\frac{H_L}{RT} \right)}{R T^2}}{(P_L \infty \exp \left( -\frac{H_L}{RT} \right) + P)^2} \quad (34)
\]

\[
\left( \frac{\partial q}{\partial T} \right)_P = -\frac{a_2 P}{T^2 \left( P_L \infty \exp \left( -\frac{H_L}{RT} \right) + P \right)} - \frac{P \cdot P_L \infty \exp \left( -\frac{H_L}{RT} \right) \cdot \left( \frac{a_2}{T^2} + a_2 \right) H_L}{R T^2 \left( P_L \infty \exp \left( -\frac{H_L}{RT} \right) + P \right)^2} \quad (35)
\]

Substituting Equations (30) and (31) in (35):

\[
\left( \frac{\partial q}{\partial T} \right)_P = -\frac{a_2 P}{T^2 (P_L + P)} - \frac{P \cdot P_L V_L H_L}{R T^2 (P_L + P)^2} \quad (36)
\]

### 6.2 Derivation of the Mass Transfer Governing Equation Accounting for Amount Adsorbed

General mass balance for porous media in the presence of adsorption is given as:

\[
\text{mass accumulation from free gas} \quad (37)
\]

\[
+ \text{mass accumulation from adsorbed gas}
\]

\[
+ \text{gas flow}
\]
\[
\phi \frac{\partial \rho_g}{\partial t} + (1 - \phi) \frac{\partial \rho_a}{\partial t} + \nabla (\rho_g \phi \mathbf{v}) = \dot{Q}_f
\]

(38)

Also, consider the definitions of isothermal compressibility and coefficient of thermal expansion [34]:

\[
c_g = \frac{1}{\rho_g} \left( \frac{\partial \rho_g}{\partial P} \right)_T
\]

(39)

\[
\alpha_g = \frac{1}{\rho_g} \left( \frac{\partial \rho_g}{\partial T} \right)_p
\]

(40)

Let's define the ratio of isothermal compressibility to the coefficient of thermal expansion as \( \gamma_g \):

\[
\gamma_g = \frac{c_g}{\alpha_g}
\]

(41)

Gas compressibility factors are calculated using Mahmoud's correlation [34]:

\[
z = (0.702 \exp(-2.5 T_{pr})) (P_{pr}^{\frac{2}{3}}) - (5.24 \exp(-2.5 T_{pr})) (P_{pr}) + (0.044 T_{pr}^{\frac{2}{3}})
\]

\[-0.164 T_{pr} + 1.15\]

(42)

Mass accumulation from free gas can now be simplified using chain rule as follows:

\[
\phi \frac{\partial \rho_g}{\partial t} = \phi \left( \frac{\partial \rho_g}{\partial P} \frac{\partial P}{\partial t} \right)_T + \phi \left( \frac{\partial \rho_g}{\partial T} \frac{\partial T}{\partial t} \right)_P
\]

(43)

From Equations (39), (40), and (43), mass accumulation from free gas is:

\[
\phi \frac{\partial \rho_g}{\partial t} = \phi c_g \rho_g \left( \frac{\partial P}{\partial t} \right)_T + \phi \alpha_g \rho_g \left( \frac{\partial T}{\partial t} \right)_P
\]

(44)

Adsorbed phase density, in moles per unit volume of shales, is reconciled with experimentally determined amount adsorbed in moles per unit mass of shales as follows:
Mass accumulation from adsorbed gas is simplified using chain rule as follows:

\[ q_a = \frac{\rho_a}{\rho_s} \]  

\[ (1 - \phi) \frac{\partial \rho_a}{\partial t} \]  

\[ = (1 - \phi) \left( \left( \frac{\partial \rho_a}{\partial P} \frac{\partial P}{\partial \rho_g} \right)_T + \left( \frac{\partial \rho_a}{\partial T} \frac{\partial T}{\partial \rho_g} \right)_p \right) \left( \left( \frac{\partial P}{\partial \rho} \frac{\partial \rho}{\partial T} \right)_T + \left( \frac{\partial T}{\partial \rho} \frac{\partial \rho}{\partial t} \right)_p \right) \]  

From equations (39), (40), (41), and (46), mass accumulation from the adsorbed phase is given as:

\[ (1 - \phi) \frac{\partial \rho_a}{\partial t} \]  

\[ = (1 - \phi) \rho_s \left[ \frac{\partial q_a}{\partial P} \right)_T + \gamma_g \frac{\partial q_a}{\partial T} \left( \frac{\partial P}{\partial \rho} \right)_T + \left[ \frac{1}{\gamma_g} \frac{\partial q_a}{\partial P} \right)_T \frac{\partial T}{\partial t} + 1 \frac{\partial q_a}{\partial T} \left( \frac{\partial \rho}{\partial t} \right)_p \frac{\partial \rho}{\partial t} \]  

Fluid velocity is Darcy velocity over porosity [12]:

\[ \vec{v} = \frac{k}{\mu \phi} \nabla P \]  

Gas flow term is therefore simplified as follows:

\[ \nabla (\rho_g \phi \vec{v}) = \nabla \left( \frac{\rho_g k}{\mu} \nabla P \right) \]  

From Equations (37), (44), (47) and (49), the pressure diffusion equation for the matrix region for variable temperature applications is given as:

\[ \left[ \phi \epsilon_g \rho_g + (1 - \phi) \rho_s \left[ \frac{\partial q_a}{\partial P} \right)_T + \gamma_g \frac{\partial q_a}{\partial T} \left( \frac{\partial P}{\partial \rho} \right)_T \right] \frac{\partial P}{\partial t} + \left[ \phi \alpha_g \rho_g - (1 - \phi) \rho_s \left[ \frac{\partial q_a}{\partial T} \right) + \frac{1}{\gamma_g} \frac{\partial q_a}{\partial P} \left( \frac{\partial \rho}{\partial t} \right)_p \frac{\partial \rho}{\partial t} \right] \frac{\partial T}{\partial t} + \nabla \left( \frac{\rho_g k}{\mu} \nabla P \right) = -Q_{if} \]
6.3 Derivation of the Heat Transfer Governing Equation Accounting for Heat of Sorption

General energy balance for porous media in the presence of adsorption is given as:

\[
\begin{align*}
\text{energy accumulation from bulk shale} & \quad (51) \\
+ \text{energy accumulation from free gas} & \\
+ \text{energy accumulation from adsorbed gas} & \\
+ \text{energy flow from conduction} & \\
+ \text{energy flow from convection} & = \text{source/sink}
\end{align*}
\]

For the shale matrix, the energy accumulation from free gas, and energy flow due to convection are 0 [19]:

\[
\begin{align*}
& (1 - \phi) \rho_s (C_{Ps}) \frac{\partial T}{\partial t} - [(1 - \phi) \rho_s H_i] \frac{\partial q_a}{\partial t} - (1 - \phi) \nabla (\lambda \Delta T) = Q_h \\
(52)
\end{align*}
\]

In terms of Pressure and Temperature:

\[
\begin{align*}
& -[(1 - \phi) \rho_s H_i \left( \frac{\partial q_a}{\partial P} \right)_T] \frac{\partial P}{\partial t} \\
& + [(1 - \phi) \rho_s C_{Ps} - (1 - \phi) \rho_s H_i \left( \frac{\partial q_a}{\partial T} \right)_P] \frac{\partial T}{\partial t} \\
& - (1 - \phi) \nabla (\lambda_s \nabla T) \\
& = (1 - \phi) Q_h \\
(53)
\end{align*}
\]

For shale pores, the energy accumulation from adsorbed gas is 0:

\[
\begin{align*}
& \phi \rho_g M W C_{Pg} \frac{\partial T}{\partial t} \\
& + \phi \rho_g M W C_{Pg} \bar{v} \cdot \nabla T \\
& - \phi \nabla \cdot (\lambda_g \nabla T) \\
& = \phi Q_h \\
(54)
\end{align*}
\]

Assuming that heat transfer occurs in series, the Equations (53) and (54) can be added to give the governing Heat Transfer Equation for Shale Matrix:
\begin{equation}
- \left[ (1 - \phi) \rho_s H_i \left( \frac{\partial q_a}{\partial P} \right)_p \left( \frac{\partial P}{\partial t} \right) \right] \\
+ \left[ \phi \rho_g MW C_{p_g} + (1 - \phi) \rho_s \left( C_p - H_i \left( \frac{\partial q_a}{\partial T} \right)_p \right) \right] \frac{\partial T}{\partial t} \\
- \nabla \cdot \left( \phi \lambda_g + (1 - \phi) \lambda_s \right) \mathbf{\nabla} T \\
+ \rho_g MW C_{p_g} \left( \frac{k_m \nabla P}{\mu} \right) \cdot \mathbf{\nabla} T
\end{equation}

= Q_h