Supporting Information (SI)

for

Heterogeneous transport of free CH$_4$ and free CO$_2$ in dual-porosity media controlled by anisotropic in-situ stress during shale gas production by CO$_2$ flooding: implications for CO$_2$ geological storage and utilization

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Key governing equations for the shale-based CGSU model development

Shale deformation is a comprehensive outcome triggered by in-situ stress, gas pressure, gas ad/desorption and thermal conduction/convection. Based on the porous elastic theory, the stress field can be described as:

\[
G u_{i,j} + \frac{G}{1-2\nu} u_{j,i} - (\alpha_u p_{m,i} + \alpha_f p_{f,i}) - K \alpha_T T^i = -K \frac{e_{1j} b_1 p_{mg1} + e_{2j} b_2 p_{mg2}}{1 + b_1 p_{mg1} + b_2 p_{mg2}} + f_k = 0 \quad (S1)
\]

where the subscript \(i\) represents the gas component (1 for CH\(_4\) and 2 for CO\(_2\)); \(u_k\) is the deformation in \(k\) direction; \(G=E/(2+2\nu)\) is the shear modulus, Pa; \(K=E/3(1-2\nu)\) is the bulk modulus, Pa; \(E\) is the Young’s modulus, Pa; \(\nu\) is the Poisson’s ratio; \(\alpha_u\) and \(\alpha_f\) are the Biot effective stress coefficient of matrix and fracture, respectively; \(p_m\) is the total gas pressure in the matrix, Pa; \(p_{mg}\) is the gas pressure in pore system, Pa; \(p_f\) is the fluid stress in the fracture, Pa; \(\alpha_T\) is the thermal expansion coefficient, \(1/K\); \(T\) is the temperature of gas, K; \(b_i=1/P_L\); \(P_L\) is the Langmuir pressure constant, Pa; \(\varepsilon_{L1}\) and \(\varepsilon_{L2}\) are the Langmuir strain coefficient of CH\(_4\) and CO\(_2\); \(f_k\) is the volume force component, N.

Based on the mass conservation law, in the dual-porosity system, the governing equation of binary gas transport is:

\[
\frac{\partial}{\partial t} (\phi_m M_w RT) p_{mg} + \frac{V_{Li} b_1 p_{mg1} + b_2 p_{mg2}}{1 + b_1 p_{mg1} + b_2 p_{mg2}} \rho_c p_{mg} \exp(-\frac{c_1}{1 + c_2 p_m}(T - T_{ref})) + \nabla \cdot (-D_i M_g \nabla \phi_m p_{mg}) = -\frac{M_g}{\tau_f RT} (p_{mg} - p_{fg}) \quad (S2)
\]

where \(M_g\) is the molar mass of gas, g/mol; \(\phi_m\) is the porosity of the shale matrix; \(R\) is gas molar constant, J/(mol·K); \(\rho_c\) is the density of the shale skeleton, kg/m\(^3\); \(\rho_{fg}\) is the density of gas under standard conditions, kg/m\(^3\); \(p_{fg}\) is the gas pressure in fracture system, Pa; \(V_{Li}\) is the Langmuir volume constant, m\(^3\)/kg; \(c_1\) and \(c_2\) are the thermal coefficients of gas sorption; \(D_i\) is the diffusion coefficient, m\(^2\)/s; \(T_{ref}\) is the reference temperature, K; \(\tau_f\) is the desorption time, s.

The two-phase flow in the fracture system is described as:
\[ \frac{\partial}{\partial t}(s \varphi_f p_{fg}) + \nabla g \cdot \rho_{fg} \left( \frac{kk_{ru}}{\mu_w} (1 + \frac{b_k}{p_{fg}}) \nabla p_{fr} \right) + \frac{\partial}{\partial t}(s \varphi_f H_g p_{fg}) = 0 \] (S3)

\[ \nabla g \cdot H_g \rho_{fg} \left( \frac{kk_{ru}}{\mu_w} \nabla p_{fr} \right) = \frac{1}{\tau_f RT} (p_{mgi} - p_{fg}) \]

where \( \varphi_f \) is the porosity of fracture; \( s_g \) is the gas saturation; \( s_w = 1 - s_g \) is the water saturation; \( p_{fg} \) is the density of gas, \( \text{kg/m}^3 \); \( H_g \) is the Henry’s coefficient of gas; \( k \) is the absolute permeability, \( \text{m}^2 \); \( k_{ru} \) and \( k_{gw} \) are the relative permeability of gas and water; \( \mu_{fg} \) and \( \mu_w \) are the dynamic viscosity of gas and water, \( \text{Pa} \cdot \text{s} \); \( b_k \) is the Klinkenberg factor, \( \text{Pa} \); \( p_{fgi} \) is the water pressure in the fracture, \( \text{Pa} \); \( p_{fg} \) is the total gas pressure in the fracture, \( \text{Pa} \); \( p_{fgw} \) is the capillary pressure, \( \text{Pa} \); \( \rho_{fg} \) is the density of water, \( \text{kg/m}^3 \); \( \rho_{fg0} \) is the density of saturated vapor, \( \text{kg/m}^3 \); \( R_i \) is the latent heat of vapor, \( \text{J/(K \cdot \text{kg})} \); \( s_{gr} \) is the residual gas saturation; \( s_{sw} \) is the irreducible water saturation.

And the relative permeability is expressed as:

\[
\begin{align*}
  k_{rg0} &= k_{rg0} (1 - \left( \frac{s_w - s_{sr}}{1 - s_{gr} - s_{sr}} \right)^2) (1 - \left( \frac{s_w - s_{sr}}{1 - s_{sr}} \right)^2) \\
  k_{gw} &= k_{gw0} \left( \frac{s_w - s_{sr}}{1 - s_{sr}} \right)^4
\end{align*}
\] (S5)

where \( k_{rg0} \) and \( k_{gw0} \) are the endpoint relative permeability of gas and water, \( s_{gr} \) is the residual gas saturation, and \( s_{sw} \) is the irreducible water saturation.

The energy exchange within a unit volume includes internal energy, heat convection and conduction, strain energy and gas adsorption heat:

\[ \frac{\partial}{\partial t} ((\rho C_p)^{\text{eff}} T) + \eta_{d} \nabla T - \nabla \cdot (\lambda_{d} \nabla T) + K_{e} T \frac{\partial \varepsilon_{e}}{\partial t} + \sum_{x=1}^{2} g_{st} \frac{\rho_{e}}{M_{gi}} \frac{\partial V_{st}}{\partial t} = 0 \] (S6)

where \( (\rho C_p)^{\text{eff}} \) is the effective heat capacity, \( \text{J/(m}^3\cdot\text{K}) \); \( \eta_{d} \) is the effective heat convection transfer coefficient, \( \text{J/(m}^2\cdot\text{s}) \); \( \lambda_{d} \) is the effective thermal conductivity, \( \text{W/(m} \cdot \text{K}) \); \( g_{st} \) is the isosteric heat of gas
adsorption, kJ/mol; \( \varepsilon_t \) is the volume strain; \( V_{\text{abs}} \) is the absorbed gas content, m\(^3\)/kg.

Therein, \( (\rho C_p)_{\text{eff}}, \eta_{\text{eff}}, \) and \( \lambda_{\text{eff}} \) are defined as:

\[
(\rho C_p)_{\text{eff}} = (1 - \varphi_m - \varphi_f) \rho C_v + \sum_{i=1}^{2} \left( s_i \varphi_f \rho C_g + \varphi_m \rho C_s + s_w \varphi_f H \rho \right) \frac{C_{\text{gi}}}{\rho C_v} + s_w \varphi_f C_v + s_0 \varphi_f \rho \exp\left( \frac{C_{\text{gi}}}{\rho C_v} \right)
\]

where \( C_v, C_g, C_s, \) and \( C_i \) are the specific heat capacities of the shale skeleton, gas, water, and vapor, J/(kg·K).

\[
\eta_{\text{eff}} = -\sum_{i=1}^{2} \left( \rho C_p \frac{\varphi_f k k_{\text{eff}}}{\mu_{\text{gi}}} \left( 1 + \frac{b_{\text{gi}}}{p_{\text{gi}}} \right) \nabla p_{\text{gi}} + \frac{H \rho C_g k k_{\text{eff}}}{\mu_{\text{gi}}} \nabla p_{\text{gi}} \right)
\]

\[
-\left( \rho \frac{\varphi_f k k_{\text{eff}}}{\rho C_v R T} \right) \sum_{i=1}^{2} \left( 1 + \frac{b_{\text{gi}}}{p_{\text{gi}}} \right) \nabla p_{\text{gi}} + \frac{\rho C_g k k_{\text{eff}}}{\mu_{\text{gi}}} \nabla p_{\text{gi}} \right)
\]

\[
\lambda_{\text{eff}} = (1 - \varphi_f - \varphi_m) \lambda_s + \varphi_m \lambda_{\text{gm}} + \varphi_f \left( s_w \lambda_{\text{fw}} + s_0 \lambda_{\text{f}} \right)
\]

where \( \lambda_s, \lambda_{\text{gm}}, \lambda_{\text{fgm}}, \) and \( \lambda_{\text{fw}} \) are the thermal conduction coefficients of the shale skeleton, gas mixture in the matrix, gas mixture in the fracture, and water in the fracture, respectively, W/(m·K).

Thereinto, as far as the CH\(_4\) and CO\(_2\) in the matrix,

\[
\lambda_{\text{gm}} = \frac{1}{2} \left( \sum_{i=1}^{2} x_i \lambda_i + \left( \sum_{i=1}^{2} x_i / \lambda_i \right)^{-1} \right)
\]

For the CH\(_4\), CO\(_2\) and vapor in the fracture,

\[
\lambda_{\text{fw}} = \frac{1}{2} \left( \sum_{i=1}^{3} x_i \lambda_i + \left( \sum_{i=1}^{3} x_i / \lambda_i \right)^{-1} \right)
\]

where \( x_i \) and \( \lambda_i \) are the molar fraction and thermal conduction coefficient of gas, respectively.

Besides, in the matrix, the porosity evolution is induced by the variation of gas pressure, temperature, and gas ad/desorption, so it can be defined as:

\[
\varphi_m = \varphi_{m0} + \frac{(\alpha_p - \varphi_{\text{ads}})(e_e - e_{\text{eq}})}{1 + \varepsilon_t}
\]

where \( e_e = e_i + p_i K_e \alpha_p \alpha_f T \varepsilon_t; \) the subscript 0 represents the initial value of parameters.

While, in the fracture, the porosity is determined by the fracture deformation:
\[ \Delta b = \frac{(\Delta \sigma_n - \alpha_j \Delta p_j)}{K_n} \quad (S13) \]

where \( \Delta b \) is the change in the fracture width, m; \( \Delta \sigma_n \) is the normal stress on the fracture, Pa; and \( K_n \) is the corresponding normal stiffness, Pa/m.

Regarding the normal stiffness, it is functioned by the normal effective stress:

\[ K_n = K_{ni}(1 - \frac{\sigma'_n}{K_{ni} \Delta v_{\text{max}} + \sigma_n})^{-2} \quad (S14) \]

where \( K_{ni} \) is the initial normal stiffness, Pa/m; \( \sigma'_n \) is the normal effective stress, Pa; and \( \Delta v_{\text{max}} \) is the maximum fracture aperture as the applied normal effective stress goes to infinity, m.

As the permeability of shale exhibits obvious anisotropic characteristic, the fracture porosity is different in the orthogonal directions based on the dual-porosity media. So, the fracture porosity is:

\[ \varphi_f = \varphi_{f0}(1 + \frac{\sum_{j=1}^{N} \Delta b_j}{b_{f0}}) \quad (S15) \]

where the subscript \( j \) represents the orthogonal direction; \( b_{f0} \) is the initial fracture width, m; and \( N \) represents the dimension – for two dimensions \( N=2 \), and for three dimensions \( N=3 \).

Furthermore, to calculate the permeability in each direction, the relationship between fracture width and permeability satisfies the cubic law:

\[ k_j = k_{j0}(1 + \frac{\Delta b_j}{b_{j0}})^3 \quad (S16) \]
| Parameter                                | Value   | Parameter                                | Value   |
|-----------------------------------------|---------|-----------------------------------------|---------|
| Initial porosity of matrix ($\phi_m$)   | 0.045   | Residual gas saturation ($\phi_{gr}$)    | 0.05    |
| Initial porosity of fracture ($\phi_f$) | 0.005   | Irreducible water saturation ($s_{wr}$)  | 0.12    |
| Gas molar constant ($K, J/(mol\cdot K)$)| 8.314   | Reference temperature ($T_{ref}, K$)    | 300     |
| Molar mass of CH$_4$ ($M_{g1}, g/mol$)  | 16      | Endpoint relative permeability of gas ($k_{rg}$) | 0.875 |
| Molar mass of CO$_2$ ($M_{g2}, g/mol$)  | 44      | Endpoint relative permeability of water ($k_{rw}$) | 1.0    |
| Langmuir volume constant of CH$_4$ ($V_L1, m^3/kg$) | 3.59e-3 | Young’s modulus ($E$, GPa) | 32.75   |
| Langmuir volume constant of CO$_2$ ($V_L2, m^3/kg$) | 11.68e-3 | Poisson’s ratio ($\nu$) | 0.235   |
| Langmuir pressure constant of CH$_4$ ($P_L1, MPa$) | 11      | Biot coefficient of matrix ($a_m$)       | 0.8     |
| Langmuir pressure constant of CO$_2$ ($P_L2, MPa$) | 8.64    | Biot coefficient of fracture ($a_f$)      | 0.1     |
| Langmuir strain coefficient of CH$_4$ ($\xi_1$) | 8.1e-4  | Density of the skeleton ($\rho_c, kg/m^3$) | 2470    |
| Langmuir strain coefficient of CO$_2$ ($\xi_2$) | 3.6e-3  | Initial fracture stiffness ($K_{fr}, GPa/m$) | 10     |
| Dynamic viscosity of CH$_4$ ($\mu_{g1}, Pa s$) | 1.34e-5 | Maximum fracture aperture ($\Delta V_{max}, m$) | 0.001 |
| Dynamic viscosity of CO$_2$ ($\mu_{g2}, Pa s$) | 1.84e-5 | Thermal expansion coefficient ($\alpha_t, 1/K$) | 2.4e-5 |
| Dynamic viscosity of water ($\mu_w, Pa s$) | 8.9e-4  | Specific heat capacities of CH$_4$ ($C_{g1}, J/(kg\cdot K)$) | 1380   |
| Diffusion coefficient of CH$_4$ ($D_1, m^2/s$) | 3.6e-12 | Specific heat capacities of CO$_2$ ($C_{g2}, J/(kg\cdot K)$) | 2220   |
| Diffusion coefficient of CO$_2$ ($D_2, m^2/s$) | 5.8e-12 | Specific heat capacities of water ($C_w, J/(kg\cdot K)$) | 4187   |
| Thermal coefficient of gas sorption ($c_t, 1/K$) | 0.021   | Specific heat capacities of vapor ($C_v, J/(kg\cdot K)$) | 1996   |
| Thermal coefficient of gas sorption ($c_t, 1/MPa$) | 0.071   | Thermal conduction coefficient of shale ($\lambda_s, W/(m\cdot K)$) | 0.1913 |
| Capillary pressure ($p_{cap}, MPa$)       | 0.035   | Thermal conduction coefficient of CH$_4$ ($\lambda_{g1}, W/(m\cdot K)$) | 0.0301 |
| Initial density of saturated vapor ($\rho_{gsv}, kg/m^3$) | 0.13    | Latent heat of vapor ($R_v, J/(K\cdot kg)$) | 461.51  |
| Latent heat of vapor ($R_v, J/(K\cdot kg)$) | 461.51  | Thermal conduction coefficient of CO$_2$ ($\lambda_{g2}, W/(m\cdot K)$) | 0.0137 |
| Klinkenberg factor ($b_{K}$, MPa)         | 0.76    | Thermal conduction coefficient of water ($\lambda_w, W/(m\cdot K)$) | 0.5985 |
| Desorption time of CH$_4$ ($\tau_1, d$)  | 0.221   | Isosteric heat of CH$_4$ adsorption ($q_{st1}, kJ/mol$) | 16.4   |
| Desorption time of CO$_2$ ($\tau_2, d$)  | 0.334   | Isosteric heat of CO$_2$ adsorption ($q_{st2}, kJ/mol$) | 19.2   |
| Henry’s coefficient of CH$_4$ ($H_{g1}$)  | 0.0014  | Initial in-situ stress ($\sigma$, MPa) | 40     |
| Henry’s coefficient of CO$_2$ ($H_{g2}$)  | 0.0347  | Initial fracture width ($b$, m) | 5e-4   |
| Initial temperature ($T_0, K$)            | 305.5   | Initial isotropic permeability ($k_i, m^2$) | 3.6e-18 |
| Initial water saturation ($s_w$)           | 0       |                                         |         |