Shale Gas Adsorption

The petrophysical model used in this document assumes that adsorbed gas occupies a portion of the pore space represented as reservoir porosity. The total mass of gas per unit bulk volume of reservoir rock can then also be expressed as

$$m_g = \phi\rho_g S_g + m_{ga} = \phi\left(\rho_g S_g + 62.428\rho_{ga} S_{ga}\right) \tag{1}$$

Note that in Eq. 1, the free gas density has units consistent with the mass of gas (lbm/ft^3), while adsorbed gas density is in g/cm^3. Ambrose *et al*. (2010) suggest a constant value of 0.37 g/cm^3 for adsorbed gas density at all reservoir pressures and temperatures.

Expressing the amount of adsorbed gas in terms of a Langmuir isotherm:

$$m_{ga} = \frac{62.428}{2000}\frac{\rho_b M_g p_{sc}}{RT_{sc}}\frac{V_L p}{p + p_L} = \frac{62.428}{2000}\rho_b \rho_g^{sc}\frac{V_L p}{p + p_L} \tag{2}$$

Or in terms of adsorbed gas saturation,

$$S_{ga} = \frac{m_{ga}}{62.428\phi\rho_{ga}} = \frac{\rho_b \rho_g^{sc}}{2000\phi\rho_{ga}}\frac{V_L p}{p + p_L} \tag{3}$$

Standard pressure and temperature used in Eqs. 3 and 4 should be consistent with the values used in the measurement of the Langmuir isotherm. A reasonable range for shale bulk density is 2.2-2.75 g/cm^3 (North, 1985).

Free and adsorbed gas in-place in Mscf/ac-ft (G_f, G_a) can also be calculated at any pressure as

$$\begin{aligned} G_f &= 43{,}560\frac{\phi}{B_g}\left(1 - S_w - S_{ga}\right) \\ &= 43{,}560\frac{\phi}{B_g}\left(1 - S_w\right) - \frac{43{,}560}{2000}\frac{\rho_b \rho_g^{sc}}{B_g \rho_{ga}}\frac{V_L p}{p + p_L} \\ &= \frac{43{,}560}{B_g}\left[\phi\left(1 - S_w\right) - \frac{\rho_b \rho_g^{sc}}{2000\rho_{ga}}\frac{V_L p}{p + p_L}\right] \end{aligned} \tag{4}$$

$$G_a = 43{,}560 \frac{62.428}{1000} \frac{\phi S_{ga} \rho_{ga}}{\rho_g^{sc}} = \frac{43{,}560 \cdot 62.428}{2000 \cdot 1000} \frac{V_L p}{p + p_L} \\ = 1.3597 \rho_b \frac{V_L p}{p + p_L} \tag{5}$$

where gas formation volume factor in Mscf/ft^3 is

$$B_g = 1000 \frac{\rho_g^{sc}}{\rho_g} = 1000 \frac{p_{sc}}{T_{sc}} \frac{zT}{p} \tag{6}$$

The ratio of adsorbed to total gas in-place is then

$$\frac{G_a}{G} = \frac{1}{1 + \frac{1000}{62.428} \frac{\rho_g^{sc}}{B_g \rho_{ga} S_{ga}} \left(1 - S_w - S_{ga}\right)} \\ = \frac{1}{1 + \frac{\rho_g \left(1 - S_w - S_{ga}\right)}{62.428 \rho_{ga} S_{ga}}} \tag{7}$$

Equation 7 evaluated at initial pressure will provide the fraction of initial gas in-place that is adsorbed.

The ratio of desorbed gas to OGIP as a function of pressure is

$$\frac{G_{ai} - G_a}{G_{fi} + G_{ai}} = \frac{\phi_i S_{ga,i} - \phi S_{ga}}{\frac{1000}{62.428} \frac{\rho_g^{sc}}{\rho_{ga}} \frac{\phi_i}{B_{gi}} \left(1 - S_{wi} - S_{ga,i}\right) + \phi_i S_{ga,i}} \tag{8}$$

Or in another form:

$$\frac{G_{ai} - G_a}{G_{fi} + G_{ai}} = \frac{1 - \frac{\phi S_{ga}}{\phi_i S_{ga,i}}}{\frac{1000}{62.428} \frac{\rho_g^{sc}}{\rho_{ga} B_{gi}} \frac{\left(1 - S_{wi} - S_{ga,i}\right)}{S_{ga,i}} + 1} \tag{9}$$

The ratio of desorbed gas to cumulative gas production is then

$$\frac{G_{ai}-G_a}{G_{fi}+G_{ai}-G_f-G_a}$$

$$=\frac{\phi_i S_{ga,i}-\phi S_{ga}}{\frac{1000}{62.428}\frac{\rho_g^{sc}}{\rho_{ga}}\left[\frac{\phi_i}{B_{gi}}\left(1-S_{wi}-S_{ga,i}\right)-\frac{\phi}{B_g}\left(1-S_w-S_{ga}\right)\right]+\phi_i S_{ga,i}-\phi S_{ga}} \tag{10}$$

Or,

$$\frac{G_{ai}-G_a}{G_{fi}+G_{ai}-G_f-G_a}=\frac{1}{\frac{1000}{62.428}\frac{\rho_g^{sc}}{\rho_{ga}}\frac{\frac{\phi_i\left(1-S_{wi}-S_{ga,i}\right)}{B_{gi}}-\frac{\phi\left(1-S_w-S_{ga}\right)}{B_g}}{\left(\phi_i S_{ga,i}-\phi S_{ga}\right)}+1} \tag{11}$$

Note that at initial conditions, this ratio is undefined. Should be set to zero.

If porosity were to be taken as only the amount of pore space occupied by free gas and water (ϕ^*) as some suggest, Eqs. 4 and 5 would become

$$G_f=43{,}560\frac{\phi^*}{B_g}\left(1-S_w\right) \tag{12}$$

$$G_a=1.3597\rho_b\frac{V_L p}{p+p_L} \tag{13}$$

The relationship between total porosity and free-gas plus water porosity is (conserving free gas in-place):

$$\phi=\phi^*+\frac{\rho_b\rho_g^{sc}}{2000\rho_{ga}\left(1-S_w\right)}\frac{V_L p}{p+p_L} \tag{14}$$

Total System Compressibility

The correct value to use for total system compressibility is one that ensures mass balance. The following can thought of as the definition of total system compressibility.

$$\frac{\partial m_g}{\partial t}=\phi\rho_g c_t\frac{\partial p}{\partial t} \tag{15}$$

Therefore total system compressibility is given by

$$c_t = \frac{1}{\phi\rho_g}\frac{\partial m_g}{\partial p} \tag{16}$$

For rock that contains both adsorbed and free gas,

$$c_t = \frac{1}{\phi\rho_g}\frac{\partial m_g}{\partial p} = \frac{1}{\phi\rho_g}\frac{\partial}{\partial p}\left(\phi\rho_g S_g + \frac{62.428}{2000}\rho_b\rho_g^{sc}\frac{V_L p}{p+p_L}\right) \tag{17}$$

Collecting terms,

$$\begin{aligned} c_t &= \frac{1}{\phi\rho_g}\frac{\partial m_g}{\partial p} = \frac{1}{\phi\rho_g}\frac{\partial}{\partial p}\left(\phi\rho_g S_g + 62.428\phi\rho_{ga}S_{ga}\right) \\ &= \frac{1}{\phi\rho_g}\frac{\partial}{\partial p}\left[\phi\rho_g\left(S_g+S_{ga}\right)+\phi S_{ga}\left(62.428\rho_{ga}-\rho_g\right)\right] \end{aligned} \tag{18}$$

Taking the two right-hand terms separately from the above:

$$\begin{aligned} RHS_1 &= \frac{1}{\phi\rho_g}\left[\phi\left(1-S_w\right)\frac{\partial\rho_g}{\partial p}+\rho_g\frac{\partial\phi\left(1-S_w\right)}{\partial p}\right] \\ &= \frac{1}{\phi\rho_g}\left[\phi\left(1-S_w\right)\frac{\partial\rho_g}{\partial p}+\rho_g\frac{\partial\phi}{\partial p}-\rho_g\frac{\partial\phi S_w}{\partial p}\right] \end{aligned} \tag{19}$$

Using the following definitions,

$$c_f \equiv \frac{1}{\phi}\frac{d\phi}{dp} = \frac{d\ln\left(\phi\right)}{dp} \tag{20}$$

$$c_g \equiv \frac{1}{\rho_g}\frac{d\rho_g}{dp} = -\frac{1}{B_g}\frac{dB_g}{dp} \tag{21}$$

$$c_w \equiv -\frac{1}{\phi S_w}\frac{d\left(\phi S_w\right)}{dp} = -\frac{d\ln\left(\phi S_w\right)}{dp} \tag{22}$$

And assuming an immobile water saturation:

$$RHS_1 = c_f + \left(1-S_w\right)c_g + S_w c_w \tag{23}$$

Assuming bulk density remains constant, the second term in Eq. 18 is then (defined as the effective compressibility correction for adsorbed state gas, c_{ga}):

$$\begin{aligned}c_{ga} &= \frac{1}{\phi\rho_g}\frac{\partial}{\partial p}\left[\phi S_{ga}\left(62.428\rho_{ga}-\rho_g\right)\right] \\ &= \frac{1}{\phi\rho_g}\left[\begin{array}{l} 62.428\rho_{ga}\left(\phi\dfrac{\partial S_{ga}}{\partial p}+S_{ga}\dfrac{\partial\phi}{\partial p}\right) \\ -\phi\rho_g\dfrac{\partial S_{ga}}{\partial p}-\phi S_{ga}\dfrac{\partial\rho_g}{\partial p}-S_{ga}\rho_g\dfrac{\partial\phi}{\partial p}\end{array}\right]\end{aligned} \tag{24}$$

Or,

$$\begin{aligned}c_{ga} &= \frac{62.428\rho_{ga}}{\rho_g}\left(\frac{\partial S_{ga}}{\partial p}+S_{ga}c_f\right)-\frac{\partial S_{ga}}{\partial p}-S_{ga}c_g-S_{ga}c_f \\ &= S_{ga}\left[c_f\left(\frac{62.428\rho_{ga}}{\rho_g}-1\right)-c_g\right]+\frac{\partial S_{ga}}{\partial p}\left(\frac{62.428\rho_{ga}}{\rho_g}-1\right) \\ &= \left(\frac{62.428\rho_{ga}}{\rho_g}-1\right)\left(S_{ga}c_f+\frac{\partial S_{ga}}{\partial p}\right)-S_{ga}c_g\end{aligned} \tag{25}$$

Noting that

$$\frac{\partial S_{ga}}{\partial p}=\frac{\rho_b\rho_g^{sc}}{2000\phi\rho_{ga}}\frac{V_L p_L}{\left(p+p_L\right)^2}=S_{ga}\frac{p_L}{p\left(p+p_L\right)} \tag{26}$$

Results in

$$c_{ga}=S_{ga}\left[\left(\frac{62.428\rho_{ga}}{\rho_g}-1\right)\left(c_f+\frac{p_L}{p\left(p+p_L\right)}\right)-c_g\right] \tag{27}$$

The effective total system compressibility is then

$$\begin{aligned}c_t &= c_f+\left(1-S_w\right)c_g+S_wc_w \\ &\quad +\frac{\rho_b\rho_g^{sc}}{2000\phi\rho_{ga}}\frac{V_L p}{p+p_L}\left[\left(\frac{62.428\rho_{ga}}{\rho_g}-1\right)\left(c_f+\frac{p_L}{p\left(p+p_L\right)}\right)-c_g\right]\end{aligned} \tag{28}$$

Or in terms of gas formation volume factor:

$$c_t = c_f + \left(1 - S_w\right) c_g + S_w c_w + \frac{\rho_b \rho_g^{sc}}{2000 \phi \rho_{ga}} \frac{V_L p}{p + p_L} \left[\left(\frac{62.428 \rho_{ga}}{1000 \rho_g^{sc}} B_g - 1 \right) \left(c_f + \frac{p_L}{p\left(p + p_L\right)} \right) - c_g \right] \tag{29}$$

To a first approximation, compressibility can be calculated by assuming a constant porosity and water saturation, varying only pressure, gas density, and compressibility. A more robust calculation would allow for porosity to change as per:

$$\phi = \phi_i \exp\left(-c_f \Delta p\right) \tag{30}$$

A similar correction to Eq. 30 can be made for water saturation:

$$S_w = S_{wi} \frac{\phi_i}{\phi} \exp\left(c_w \Delta p\right) = S_{wi} \exp\left[\left(c_f + c_w\right) \Delta p\right] \tag{31}$$

Nomenclature

B_g = gas formation volume factor, ft^3/Mscf

B_{ga} = formation volume factor of adsorbed gas, ft^3/Mscf

c_f = pore volume compressibility, psi^{-1}

c_g = gas compressibility, psi^{-1}

c_{ga} = effective adsorbed gas compressibility, psi^{-1}

c_t = total system compressibility, psi^{-1}

c_w = water compressibility, psi^{-1}

m_g = gas mass per unit reservoir bulk volume, lbm/ft^3

m_{ga} = adsorbed gas mass per unit reservoir bulk volume, lbm/ft^3

M_g = gas molecular weight, lbm/lbmol

p = pressure, psia

p_L = Langmuir pressure, psia

p_{sc} = standard pressure, psia

R = universal gas constant, psia·ft^3/lbmol/R

R_{ga} = ratio of adsorbed to free gas density

S_g = gas saturation, fraction

S_w = water saturation, fraction

T_{sc} = standard pressure, psia

V_b = bulk reservoir volume ft^3

V_L = Langmuir volume, scf/ton

z = gas deviation faction, dimensionless

ϕ = porosity, fraction

ϕ_a = porosity occupied by adsorbed gas, fraction

ϕ_v = porosity occupied by free gas and connate water, fraction

$\gamma_{g,a}$ = specific gravity of adsorbed gas, fraction

ρ_b = bulk shale density, g/cm^3

ρ_g = gas density, lbm/ft^3

ρ_{ga} = adsorbed gas density, g/cm^3

ρ_g^{sc} = gas density at standard conditions, lbm/scf

ρ_w^{sc} = density of water at standard conditions, 62.368 lbm/ft^3

References

Ambrose, R. J., Hartman, R. C., Campos, M. D., Akkutlu, I. Y., & Sondergeld, C. (2010). New Pore-scale Considerations for Shale Gas in Place Calculations. In *SPE Unconventional Gas Conference*. Pittsburgh, Pennsylvania, USA: Society of Petroleum Engineers.

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