Appendix A  Calculation of Hydrate Saturation for Excess Gas Experiments

Excess Gas Experiments

1. Loading the partially water saturated sediment in the cell, compacting by applying an overburden pressure of 3.5 MPa, and injecting methane gas, the total volume of the system is given by:

\[ V_o = V_{geo} + V_s \]  

(A.1)

Where \( V_o \) is the initial volume of the system, \( V_{geo} \) is the volume of methane gas injected, and \( V_s \) is the volume occupied by sand.

Since a known mass of gas is injected, the mole of gas is also known and represented as \( n_{geo} \). Thus, \( V_{geo} \) can be estimated by:

\[ V_{geo} = \frac{Z_o n_{geo} RT_o}{P_o} \]  

(A.2)

Since \( V_{geo} \) is the volume of the gas injected and it occupies the available pore spaces, it is considered as the pore volume. Volume occupied by sand can therefore be estimated as:

\[ V_s = V_o - V_{geo} \]  

(A.3)

2. Allowing the system to stabilise immediately after gas injection, the new cell volume becomes:

\[ V_1 = V_{geo} + V_s \]  

(A.4)
Appendix A: Calculation of Hydrate Saturations for Excess Gas Experiments

Methane solubility in water is low, and could be taken to be negligible given the short time. Thus \( n_{gg1} = n_{gg0} \), then the volume of methane gas at the new temperature and pressure is:

\[
V_{gg1} = \frac{Z_1 n_{gg1} RT_1}{P_1}
\]

When the system reaches equilibrium without hydrate formation, the new cell volume becomes:

\[
V_2 = V_{gg2} + V_s
\]

Given the length of time taken to reach equilibrium, there would be significant methane dissolution in water, thus \( n_{gg2} \neq n_{gg1} \), and \( V_{gg2} = V_2 - V_s \), then \( n_{gg2} \) can be estimated by:

\[
n_{gg2} = \frac{P_2 V_{gg2}}{Z_2 RT_2}
\]

The amount of methane gas dissolved in water can be estimated as:

\[
\Delta n = n_{gg1} - n_{gg2} = \left( \frac{P_1 V_{gg1}}{Z_1 RT_1} - \frac{P_2 V_{gg2}}{Z_2 RT_2} \right)
\]

This will however not be used in the calculations.

3. Setting the system to hydrate formation temperature and allowing time for hydrate formation. During hydrate formation, water is converted to hydrate. Thus, the volume of the remaining free water can be represented as \( V_w \). The new cell volume after hydrate formation is:

\[
V_3 = V_w + V_{gg3} + V_h + V_s
\]

Where \( V_h \) is the volume of hydrate.

To estimate \( V_h \), the unknown parameters, \( V_w \) and \( V_{gg3} \) need to be estimated.

**Estimation of** \( V_w \)
If $m_{w,tot}$ is the total mass of water in the system, it is necessary to know how much of $m_{w,tot}$ is converted to hydrate. From stoichiometry, one mole of methane hydrate is composed of one mole of methane and $n_h$ mole of water. $n_h$ is the hydration number. For the tests, a hydration number of 6 which is commonly used is adopted.

$$CH_4n_H_2O = CH_4 + n_H_2O$$

Then, it can be written that:

$$m_h = m_{wh} + m_{gh} \quad \text{A.10}$$

Where $m_h$ is the mass of methane hydrate formed, $m_{wh}$ is the mass of water consumed for hydrate formation, and $m_{gh}$ is the mass of gas consumed for hydrate formation.

The hydration number $n_h$ is defined as:

$$n_h = \left( \frac{m_{gh}}{M_g} \right) \left( \frac{m_{wh}}{M_w} \right)^{-1} \quad \text{A.11}$$

Where $M_g$ and $M_w$ are the molecular weights of methane gas and water respectively.

Substituting equation A.11 into equation A.10 and re-arranging for $m_{gh}$, $m_{wh}$, and $n_{gh}$ respectively:

$$m_{gh} = \left( 1 + \frac{1}{n_h M_g} \right)^{-1} m_h \quad \text{A.12}$$

$$n_{gh} = \left( 1 + \frac{1}{n_h M_g} \right)^{-1} m_h \quad \text{A.13}$$
Appendix A: Calculation of Hydrate Saturations for Excess Gas Experiments

\[ m_{wh} = \left( 1 + n_h \frac{M_g}{M_w} \right)^{-1} m_h \]  \hspace{1cm} A.14

Therefore,

\[ V_w = \frac{(m_{w,\text{tot}} - m_{wh})}{\rho_w} \]  \hspace{1cm} A.15

\[ V_w = \frac{1}{\rho_w} \left( m_{w,\text{tot}} - \left( 1 + n_h \frac{M_g}{M_w} \right)^{-1} m_h \right) \]  \hspace{1cm} A.16

Noting that \( m_h = \rho_h V_h \), it can be written that:

\[ V_w = \frac{1}{\rho_w} \left( m_{w,\text{tot}} - \left( 1 + n_h \frac{M_g}{M_w} \right)^{-1} V_h \rho_h \right) \]  \hspace{1cm} A.17

**Estimation of \( V_{rg} \)**

Total mole of methane gas in solution with water at the end of hydrate formation is estimated as:

\[ n_{gw} = \frac{S}{1 - S} \frac{(m_{w,\text{tot}} - m_{wh})}{M_w} \]  \hspace{1cm} A.18

Where \( S \) is the solubility of methane in water.

Substituting equation A.14 into equation A.18

\[ n_{gw} = \frac{S}{M_w (1 - S)} \left( m_{w,\text{tot}} - \left( 1 + n_h \frac{M_g}{M_w} \right)^{-1} m_h \right) \]  \hspace{1cm} A.19

It is also known that:
Appendix A: Calculation of Hydrate Saturations for Excess Gas Experiments

Total mole of gas injected = mole of gas dissolved in water + mole of free gas + mole of gas converted to hydrate, ie.

\[ n_{g,1} = n_{g,w} + n_{g,3} + n_{g,h} \]  

Therefore:

\[ n_{g,3} = n_{g,1} - n_{g,w} - n_{g,h} \]

\[ V_{g,3} = \frac{Z_3 n_{g,3} RT_3}{P_3} \]

Then:

\[ V_{g,3} = \frac{Z_3 RT_3}{P_3} (n_{g,1} - n_{g,w} - n_{g,h}) \]

Estimation of \( V_h \)

Substituting equations A.13 and A.19 into equation A.23, and putting \( m_h = V_h \rho_h \):

\[
V_{g,3} = \frac{Z_3 RT_3}{P_3} \left( \frac{P V_{g,1}}{Z_1 RT_1} - \frac{S}{M_w (1 - S)} \left( m_{w,tot} - \left( 1 + \frac{M_g}{M_w} \right)^{-1} \right) \left( 1 + \frac{1}{M_g} \left( 1 + \frac{1}{n_h M_g} \right)^{-1} \right) \right) V_h \rho_h \]

Putting \( V_{g,3}, V_w, V_3, V_s \) into equation A.9 and re-arranging for \( V_h, V_h \) can be calculated as:
Appendix A: Calculation of Hydrate Saturations for Excess Gas Experiments

\[
V_h = \frac{V_3 - V_1 - \frac{m_{w, tot}}{\rho_w} - \frac{Z_iRT_i}{P_1} \left( \frac{PV_{g \rightarrow g}^1}{RT_i} - \frac{S}{M_g (1 - S)}m_{w, tot} \right)}{1 - \frac{\rho_h}{\rho_w} \left( 1 + n_h \frac{M_g}{M_w} \right)^{-1} - \frac{Z_iRT_i}{P_3} \left( \frac{1}{M_g} \left( 1 + \frac{1}{n_h} \frac{M_g}{M_w} \right)^{-1} - \frac{S}{M_g (1 - S)} \left( 1 + n_h \frac{M_g}{M_w} \right)^{-1} \right) \rho_h}
\]

Given \( V_h \), methane hydrate saturation can be estimated as:

\[
S_h = \frac{V_h}{V_h + V_w + V_{gg}}
\]