Supplementary Appendix SA1: Calculation of hydrate saturation

In this study, methane hydrate, water and gas fill the voids of glass-beads in a constant volume reactor, the hydrate saturation is defined as the volume ratio of the hydrate V_h and the pore volume V_p in a porous medium.

In the physical model, S_h can be calculated based on the volume conservation. The total volume of water and methane gas before hydrate formation is equal to that of water, gas and hydrate in the reactor after hydrate formation (Jin et al., 2018; Li et al., 2014; Li et al., 2012a; Zhao et al., 2015). Therefore, the volume conservation can be expressed as:

$$V_p = V_{w0} + V_{g0} = V_{w1} + V_{g1} + V_h \quad (1)$$

where V_{w0} and V_{g0} are the volume of water and CH_4 under initial conditions of pressure (P_0) and temperature (T_0), respectively; V_{w1}, V_{g1} and V_h are the volumes of water, CH_4 and methane hydrate under the finial conditions of pressure (P_1) and temperature (T_1), respectively.

In addition, it is assumed that hydrate is formed homogeneously in the BZ-01 glass-beads; water in the reactor is incompressible and expansion of the reactor is ignored; the molecular structure of methane hydrate is $CH_4 \cdot 6H_2O$; under the standard condition, 164 Sm^3 of CH_4 gas and 0.8 m^3 of water can be obtained from 1 m^3 of hydrate dissociation.

Based on the real gas law, V_{g0} and V_{g1} can be expressed as follows:

$$V_{g0} = \frac{0.1 Z_0 T_0 V_{gs0}}{273.15 P_0} \quad (2)$$

$$V_{g1} = \frac{0.1 Z_1 T_1 (V_{gs0} - V_{gs})}{273.15 P_1} \quad (3)$$

Combining Equations (1) - (3), we obtain the total formula as follows:

$$V_{w0} + \frac{0.1 Z_0 T_0 V_{gs0}}{273.15 P_0} = \frac{V_{w1}\rho_w - \frac{V_{gs}\rho_h}{164} + V_{gs}\rho_g}{\rho_w} + \frac{V_{gs}}{164} + \frac{0.1 Z_1 T_1 (V_{gs0} - V_{gs})}{273.15 P_1} \quad (4)$$

where Z_0 and Z_1 are the gas compressibility factors according to different conditions of pressure and temperature, V_{gs0} is the standard volume of gas before hydrate formation, V_{gs} is the volume of gas transferred into methane hydrate, ρ_w, ρ_g and ρ_h are the densities of water, methane gas and methane hydrate, respectively. V_{w0}, V_{gs0}, P_0, T_0 and P_1, T_1 could be measured in the experiment of hydrate formation, V_{gs} can be solved by the Equation (4). Thus, hydrate saturation can be calculated as the following equation:

$$S_h(\%) = \frac{V_h}{V_p} \times 100 = \frac{V_{gs}}{164 V_p} \times 100 = \frac{V_{gs}}{164 V \emptyset} \times 100 \quad (5)$$

where V is the volume of reactor cavity, $\emptyset$ is porosity of glass-beads.