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# Simulating the chemical kinetics of CO<sub>2</sub>-methane exchange in hydrate

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## Abstract

Carbon dioxide exchange with methane in the clathrate structure has been shown beneficial in laboratory experiments and has been suggested as a field-scale technique for production of natural gas from gas-hydrate bearing sediments. Furthermore, the method is environmentally attractive due to the formation of CO<sub>2</sub>-hydrate in the sediments, leading to the geosequestration of carbon dioxide. However, the knowledge is still limited on the impact of small-scale heterogeneities on hydrate dissociation kinetics. In the present study, we developed a model for simulating laboratory experiments of carbon dioxide injection into a pressure vessel containing a mixture of gas hydrate and quartz sand. Four experiments at different temperature and pressure conditions were modeled. The model assumes that the contents are ideally mixed and aims to estimate the effective dissociation rate of gas hydrate by matching the model results with the experimental observations. Simulation results indicate that with a marginal offset the model was able to simulate different hydrate dissociation experiments, in particular, those that are performed at high pressures and low temperatures. At low pressures and high temperatures large discrepancies were noticed between the model results and the experimental observations. The mismatches were attributed to the development of extremely heterogeneous flow patterns at pore-scale, where field-scale models usually assume the characteristics to be uniform. Through this modeling study we estimated the irreversible dissociation rate of methane- and CO<sub>2</sub>-hydrate as 0.02 and 0.03 mol.m<sup>-3</sup>s<sup>-1</sup>, respectively.

**Keywords:** *CO<sub>2</sub> injection; CO<sub>2</sub>-methane exchange; Gas-hydrate recovery; Small-scale heterogeneities; Kinetic modeling*

## 23 1 Introduction

24 Gas-hydrates are solid clathrate compounds that are thermodynamically stable at low temper-  
25 atures and high pressures. Such conditions naturally exist below permafrost and in deep ocean  
26 sediments in which immense amount of methane is estimated to be stored as gas-hydrate de-  
27 posits (Archer et al., 2009; Burwicz et al., 2011). The global amount of gas-hydrate deposits  
28 have been reported between  $10^{15}$  and  $10^{18}$  standard cubic meters (Piñero et al., 2013; Wallmann  
29 et al., 2012), or about 15 Tera tonnes of oil equivalent (Makogon, 2010) which is adequate for  
30 maintaining the supply of energy for centuries. Although the range of estimates is wide, it is  
31 agreed that the available amount of gas-hydrate deposits is huge and thus worth of the atten-  
32 tion as an alternative source of energy. Development of strategies for extraction of methane  
33 from gas-hydrate reservoirs has recently become an economically attractive option given the  
34 environmental desirability of natural gas as a fuel in comparison to other fossil fuels.

35 Methods of producing natural gas from gas-hydrates are mainly based on disturbing the ther-  
36 modynamic stability of gas-hydrate in the reservoir leading to dissociation of the gas-hydrate  
37 and release of the methane. The methods include (i) thermal stimulation by increasing the tem-  
38 perature in the reservoir (e.g., Fitzgerald and Castaldi, 2013), (ii) depressurization (e.g., Ahmadi  
39 et al., 2007), (iii) hydrate conversion by substituting gas molecules inside the gas-hydrate crystals  
40 with another similar gas (e.g., Kvamme et al., 2007, 2016; Ohgaki et al., 1996), and (iv) injection  
41 of thermodynamic inhibitors (e.g., amino acids, salts, alcohols or non-ionic surfactants) (Erfani  
42 et al., 2017; Masoudi and Tohidi, 2005) for altering phase equilibrium conditions. Amongst all  
43 these methods, the conversion of methane-hydrate to  $\text{CO}_2$ -hydrate by injection of  $\text{CO}_2$  has par-  
44 ticularly attracted attentions since carbon dioxide is shown to be able to displace methane in the  
45 hydrate lattice provided that both gases form a similar hydrate structure (type SI) (Kvamme  
46 et al., 2016; Ohgaki et al., 1996; Voronov et al., 2014). The replacement of guest molecules can  
47 happen either directly without dissociation of the hydrate structure or indirectly through con-  
48 secutive dissociation of methane-hydrate and formation of  $\text{CO}_2$ -hydrate. Goel (2006) discussed  
49 that the introduction of carbon dioxide to the reservoir and its conversion to hydrate is alone suf-  
50 ficient to thermodynamically maintain the dissociation of methane-hydrate. The  $\text{CO}_2$ -methane  
51 exchange, regardless of its exchange mechanism, is particularly interesting for its capacity to  
52 sequester carbon dioxide in favor of reducing greenhouse gas emissions (see e.g., Dashti et al.,  
53 2015; Kvamme et al., 2007). The method also has a couple of other side benefits such as main-

54 taining the mechanical stability of the reservoir preventing sea-floor landslides in field operations  
55 (Sultan et al., 2004), and the potential for thermal stimulation through the injection of super-  
56 critical carbon dioxide (Deusner et al., 2012; Ebinuma, 1993). The feasibility of CO<sub>2</sub>-methane  
57 exchange as a technology to produce natural gas from gas-hydrate zones has already been pro-  
58 posed and investigated (e.g., Yonkofski et al., 2016). Many other studies, e.g., Kvamme et al.  
59 (2016); Deusner et al. (2012); Ota et al. (2005), analyzed the outcome of CO<sub>2</sub>-methane exchange  
60 at laboratory scale using apparatuses in which carbon dioxide (either gas or liquid) is injected  
61 into a vessel containing methane-hydrate. A substantial number of studies have used numerical  
62 models to evaluate the conventional methods of production from gas-hydrate reservoirs (e.g.,  
63 Moridis and Reagan, 2011a,b; Vafaei et al., 2014). However, numerical studies on CO<sub>2</sub>-methane  
64 exchange are few and are mostly limited to the field-scale. For example, White et al. (2011)  
65 modeled the injection of carbon dioxide into a depressurized gas-hydrate reservoir and stated  
66 that the low injection pressures of carbon dioxide can enhance the methane recovery from class  
67 1 hydrate.

68 Although significant research efforts have been dedicated to the development of efficient ex-  
69 perimental procedures and reliable models[they may ask for references], the complex reaction  
70 kinetics of CO<sub>2</sub>-methane exchange at the scales of pore to core has not yet been addressed in  
71 detail or experimentally constrained under the controlled conditions. Most of current modeling  
72 approaches [e.g. ???] simplify the reaction kinetics (usually employ a simple first-order kinet-  
73 ics) and neglect the small-scale heterogeneities at the scale of their computational grid (where  
74 the transport properties are averaged and considered constant).

75 In contrast to the existing modeling studies that mostly concentrated on complexity of  
76 fluid dynamics at large scales (and simplified the reaction kinetics due to uprising numerical  
77 instabilities), the present model focuses on complexity of the reaction kinetics and simplifies  
78 the fluid flow mechanisms. To this end, the approach provides a measure to gauge the lone  
79 importance of kinetics at small scales where heterogeneities are typically ignored. The overall  
80 aim is thus to use the numerical simulations to unravel the extent of influence that typical  
81 assumptions of simplifying reaction kinetics and ignoring pore-scale heterogeneities have on the  
82 accuracy of estimations at small scales, and to illustrate the contributions of error to field-scale  
83 modeling calculations. Are you sure about the word uprising above? Furthermore, the  
84 present study evaluates the reported rate values of hydrate dissociation and formation in the

85 literature and approximates/testifies the effective rate parameter values for the experimental  
86 results of [Deusner et al. \(2012\)](#). For this purpose, a rigorous optimization technique ([Babaei  
87 and Pan, 2016](#)) was applied to fit the model to the experimental results.

88 The paper is structured as follows: first we describe the model structure and its underlying  
89 assumptions. Then, the governing equations of hydrate dissociation/formation kinetics, mass  
90 and energy balance are introduced. Next, we describe the optimization formulation to calibrate  
91 the system kinetics using existing experimental data from [Deusner et al. \(2012\)](#). Finally, results  
92 are presented and discussed.

## 93 2 Experimental Setup

94 [Deusner et al. \(2012\)](#) examined methane production from hydrates by injection of supercritical  
95 carbon dioxide into a pressure vessel containing a water-saturated mixture of methane-hydrate  
96 and quartz sand. The experiments were performed at four different pressure-temperature con-  
97 ditions that are typical for naturally formed gas-hydrate reservoirs (Fig. 1).

98 The sediment samples were prepared at -20 °C from a homogeneous mixture of quartz sand  
99 (grain size of 0.1-0.6 mm) and fine ice particles (grain size fraction of 0.3-1 mm) produced from  
100 deionized water. Experiments were carried out in a custom-made high pressure stainless steel  
101 apparatus. Supercritical CO<sub>2</sub> was injected with a piston pump from an inlet at the bottom of  
102 the sample vessel and was heated to 95 °C inside temperature controlled conditioning chamber  
103 prior to the injection. Pressure, salinity and temperature were continuously monitored and  
104 recorded at the inlet and outlet. To achieve a constant rate of injection, pressure was adjusted  
105 with a back-pressure regulator valve in line with a fine-regulating valve for the compensation of  
106 pressure spikes. At the beginning of every CO<sub>2</sub> injection interval, the sediment-hydrate sample  
107 was continuously percolated with saltwater at a flow rate of 1.0 ml.min<sup>-1</sup>. The water pre-wash  
108 was performed to ensure that the sample body was permeable and homogeneously pressurized.  
109 CO<sub>2</sub> was injected stepwise following a sequential injection strategy and completed after a four  
110 to six injection rounds with CO<sub>2</sub> supply rates of 2.5 to 5 ml.min<sup>-1</sup>. The waiting time between  
111 the injection intervals are referred to as equilibration intervals during which no effluent fluid was  
112 produced and the system was left to reach thermodynamic equilibrium. During the equilibration  
113 intervals, the system pressure was maintained by the injection of a small amount of CO<sub>2</sub> in order  
114 to compensate the volume changes due to CO<sub>2</sub> cooling and phase changes. The CO<sub>2</sub> injection

115 intervals and the waiting time between them were different for each experiment.

116 Experiments were performed at three ambient temperatures (2, 8 and 10 °C). The temper-  
117 ature was regulated at the exterior surface of the vessel with a thermostat system and kept  
118 constant through the entire experiment. At the start of experiment, the vessel included only  
119 three components: methane, water and quartz sand. Methane and water initially existed as  
120 methane-hydrate. The quartz sand was assumed nonreactive and regarded as an inert solid  
121 phase. During injection intervals, the introduction of hot CO<sub>2</sub> altered the system thermody-  
122 namics and new additional components such as liquid CO<sub>2</sub> and gaseous methane were identified  
123 (Fig. 2). CO<sub>2</sub>-hydrate formation was also viable depending on system p/T conditions during  
124 equilibration. It was impossible to exactly determine the final composition of gas-hydrate at the  
125 end of the experiments. There is, however, a high possibility that a mixed CO<sub>2</sub>-CH<sub>4</sub>-hydrate  
126 was formed in the vessel. Nevertheless, the mixed composition of gas-hydrates could not influ-  
127 ence the mass balance calculations which were done based on component inventories and by the  
128 volume balancing of inputs and outputs. See [Deusner et al. \(2012\)](#) for further details about the  
129 experiments and the assembly of apparatus.

### 130 3 Materials and Methods

131 The model describes the experimental pressure vessel as an isobaric perfectly mixed reactor. In  
132 this modeling approach, the system was considered homogeneous and the chemical components  
133 inside it were assumed ideally mixed.

134 In the model, superheated liquid CO<sub>2</sub> entered from the inlet during the injection periods  
135 and dissociates the methane-hydrate in place. Then the system is left to reach the equilibrium  
136 and this cycle repeats for several times according to the experimental procedure. Given that  
137 the vessel pressure was kept constant during the entire experiment, the mobile substances (e.g.,  
138 water, CO<sub>2</sub> and methane) were allowed to discharge from the outlet during the injection intervals  
139 only. The outlet composition was assumed identical to the composition of the substances inside  
140 the reactor, which itself is a function of residence time and the reaction kinetics. Depending on  
141 the p/T conditions in the vessel, CO<sub>2</sub>- or methane-hydrate could form during the equilibrium  
142 intervals. The terms CO<sub>2</sub>-hydrate and methane-hydrate in this modeling study represent the  
143 components CO<sub>2</sub> and methane incorporated in the gas-hydrate phase. The thermodynamics of  
144 mixed gas-hydrates is not explicitly considered in the model.

## 145 3.1 Governing equations

### 146 3.1.1 Mass balance

147 System mass balance follows the equation (COMSOL 4.3, 2013),

$$\frac{d(c_j V_r)}{dt} = v_j c_{i,j} - v_j c_j + r_j V_r \quad (1)$$

148 where  $V_r$  is the volume of reactor,  $c_j$  is the concentration of substance  $j$  (Water, CO<sub>2</sub>, methane,  
149 etc.) in the system,  $c_{i,j}$  is the concentration of substance  $j$  at the inlet,  $v_j$  is the rate of influent  
150 stream to the system (equal to effluent) and  $r_j$  is the increase/decay rate of substance  $j$  according  
151 to the reactions.

### 152 3.1.2 Energy balance

153 The solution of energy balance gives (COMSOL 4.3, 2013):

$$V_r \sum_j c_j C_{p,j} \frac{dT}{dt} = Q_r + Q_w + \sum_j v_j c_{i,j} (h_{i,j} - h_j) \quad (2)$$

154 where  $h_j$  is the enthalpy of substance  $j$ ,  $C_{p,j}$  the heat capacity of substance  $j$ ,  $Q_w$  the amount  
155 of energy lost or gained through the reactor walls, and  $Q_r$  the energy consumed or released by  
156 reactions,

$$Q_r = V_r \sum_k H_k r_k \quad (3)$$

157 with  $H_k$  as the enthalpy of reaction  $k$ .  $Q_w$  is calculated analytically for the cylindrical shape of  
158 reactor:

$$Q_w = 2\pi L \lambda_m (T_s - T) \quad (4)$$

159 where  $T$  is the system temperature,  $L$  the length of vessel, and  $T_s$  is the temperature at the  
160 inner surface of reactor wall calculated by

$$T_s = \frac{\lambda_m T + \lambda_w T_w}{\lambda_m + \lambda_w} \quad (5)$$

161 with  $\lambda_m$  and  $\lambda_w$  calculated as,

$$\lambda_m = \frac{\kappa_m}{\ln(r_s/r_{in})}, \lambda_w = \frac{\kappa_w}{\ln(r_o/r_s)} \quad (6)$$

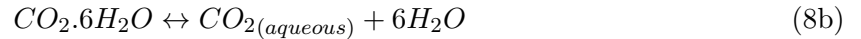
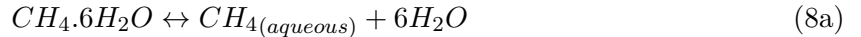
162 where  $r_s$  is the reactor inner radius,  $r_{in}$  is the radius of inlet,  $r_o$  is the reactor outer radius,  $\kappa_w$  is  
 163 the thermal conductivity of the wall material and  $\kappa_m$  is the overall thermal conductivity of the  
 164 system calculated by  $\kappa_m = \sum s_j \kappa_j$  where  $\kappa_j$  is the thermal conductivity and  $s_j$  is the saturation  
 165 of substances inside the vessel calculated by  $s_j = c_j \phi M_j / \rho_j$ .  $\phi$  is the porosity of vessel,  $M_j$  is the  
 166 molecular weight and  $\rho_j$  is the density of substance  $j$ . The enthalpy of substances at different  
 167 system temperatures are calculated as,

$$h_j(T) = \int_0^T C_{p,j} dT + h_j(0) \quad (7)$$

168 where  $h_j(0)$  is the enthalpy of substance  $j$  at a reference temperature and pressure.  $h_j(0)$  values  
 169 at 293K and 13MPa for methane, CO<sub>2</sub> and water were calculated 12.25, 10.5 and 1.72 kJmol<sup>-1</sup>  
 170 respectively (NIST Chemistry WebBook, [Linstrom and Mallard, 2013](#)).  $C_{p,j}$  was assumed con-  
 171 stant for the p/T conditions of experiments.

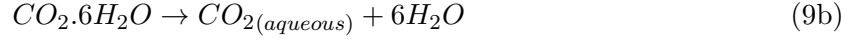
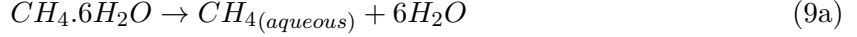
### 172 3.1.3 Reactions

173 The solution of mass and energy balance considers the following reactions inside the reactor.  
 174 Depending on the p/T conditions, hydrate dissolution and formation occur inside the hydrate  
 175 stability region and hydrate dissociation occurs outside the hydrate stability region (see Fig. 1).  
 176 The following pair of reversible reactions were considered under the stability conditions:



177 Reactions [8a-8b](#) account for hydrate dissolution while thermodynamically stable, but under-  
 178 saturated with respect to the gas in the solution (water). Hydrate precipitation (formation)  
 179 occurs at over-saturated conditions. A set of irreversible reactions were considered for p/T  
 180 conditions at which hydrates are thermodynamically unstable,





181 Reactions 9a and 9b account for disintegration of hydrate when it is not stable. Since during the  
 182 experiments the pressure of the system was kept constant, the stability of hydrates in model was  
 183 determined only by the system temperature. The hydrate instability occurred when the system  
 184 temperature exceeded the hydrate stability temperature  $T_c$ . For the experiments at 13MPa,  
 185 the stability temperatures for CH<sub>4</sub>-/CO<sub>2</sub>-hydrate were measured from stability curves (Fig. 1)  
 186 at 13.7/9.5 °C, respectively. These values were lower for the experiment at 8MPa and were  
 187 determined to be 8.95 and 8.9 °C for CH<sub>4</sub>- and CO<sub>2</sub>- hydrate, respectively.

188 According to [Haeckel et al. \(2004\)](#) the rate of hydrate dissolution/formation  $r_j$  was calculated  
 189 by,

$$r_j = \begin{cases} k_{rev,j}(c_{cte,j} - c_{Hydrate_j}) & \text{if } T < T_c, \\ k_{irr,j} & \text{if } T > T_c. \end{cases} \quad (10a)$$

$$r_j = \begin{cases} k_{rev,j}(c_{cte,j} - c_{Hydrate_j}) & \text{if } T < T_c, \\ k_{irr,j} & \text{if } T > T_c. \end{cases} \quad (10b)$$

190 Under hydrate stability condition,  $k_{rev,j}$  is defined based on the Arrhenius formula,

$$k_{rev,j} = A_j e^{-\frac{\Delta E_j}{R_c T}} \quad (11)$$

191 where  $T$  is the system temperature,  $R_c$  is the universal gas constant, and for hydrate  $j$ ,  $A_j$   
 192 denotes the frequency factor and  $\Delta E_j$  the activation energy (Table 1).  $A_j$  is typically expressed  
 193 in [mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>] and to convert its unit to [s<sup>-1</sup>] the following equation is used ([Kim et al.,](#)  
 194 [1987](#)):

$$A_j[s^{-1}] = \frac{6P_{sys}}{\Psi \rho_j d_j} A_j[mol m^{-2} s^{-1} Pa^{-1}] \quad (12)$$

195 where  $d_j$  is the average diameter of hydrate particles,  $P_{sys}$  is the system pressure,  $\rho_j$  is the hydrate  
 196 molar density, and  $\Psi$  is the particles geometry term ( $\Psi = 1$  for spherical particles). According  
 197 to [Haeckel et al. \(2004\)](#), Eq. (10) assumes hydrate dissolution or formation to be proportional to  
 198 the saturation of methane in pore water with respect to its equilibrium concentration ( $c_{cte}$ ). At

199 hydrate instability conditions (at system temperatures above the stability temperature)  $k_{irr,j}$   
 200 was assumed constant and treated as an adjustable parameter.

201 The exchange rate of methane and CO<sub>2</sub> from pure phase to the water phase and vice-versa  
 202 is defined by the following reversible reactions,



203 where the exchange rates follow the same mechanism as of Eq. (10) without the temperature  
 204 dependencies, and similar to [Noyes et al. \(1996\)](#),

$$r_j = k_{s,j}(c_{cte,j} - c_j).$$

205 The exchange rate constants  $k_{s,j}$  are estimated by the fitting procedure. The values of  $c_{cte}$   
 206 for aqueous CO<sub>2</sub> and methane, and both CO<sub>2</sub>- and CH<sub>4</sub>-hydrates at experimental temperatures,  
 207 pressures and salinity are calculated according to Henry's law and listed in [Table 1](#).

### 208 3.2 Optimization technique

209 Interior-reflective Newton methods ([Coleman and Li, 1996](#); [Gharasoo et al., 2017](#)) which are  
 210 often employed in solving optimization problems have difficulties in minimizing this model due  
 211 to high nonlinearity and discontinuity of the objective function. We thus used a hybrid response  
 212 surface surrogate-based method which also reduces the computation costs of the optimization  
 213 process. The details of the algorithm is presented in [Babaei and Pan \(2016\)](#) where the authors  
 214 showed that the surrogate model that most consistently and robustly results in a computationally  
 215 efficient optimization operation is the Radial Basis Function (RBF).

216 We first define normalized root-mean-square derivations (NRMSD) for inventory CH<sub>4</sub> and  
 217 CO<sub>2</sub> as functions of four unknown parameters  $k_{irr,MGH}$  ,  $k_{irr,CGH}$  ,  $k_{s,CH4}$  , and  $k_{s,CO2}$ :

$$\text{NRMSD}_{CO_2} = \frac{\sqrt{\mathbf{E}((CO_2^{inv.}) - (CO_2^{inv.exp}))^2)}}{\max(CO_2^{inv.exp}) - \min(CO_2^{inv.exp})} \quad (14a)$$

$$\text{NRMSD}_{CH_4} = \frac{\sqrt{\mathbf{E}((CH_4^{inv.}) - (CH_4^{inv.exp}))^2)}}{\max(CH_4^{inv.exp}) - \min(CH_4^{inv.exp})} \quad (14b)$$

218 where  $\mathbf{E}$  is the mean square error function,  $CO_2^{inv.}$ ,  $CO_2^{inv.exp}$ ,  $CH_4^{inv.}$ , and  $CH_4^{inv.exp}$   
 219 are respectively the inventory  $CO_2$  calculated from the numerical model, inventory  $CO_2$  calcu-  
 220 lated from experiment, inventory  $CH_4$  calculated from the numerical model and inventory  $CH_4$   
 221 calculated from experiment. The objective function to be minimized is written as

$$\mathbf{f}(k_{irr,MGH}, k_{irr,CGH}, k_{s,CH_4}, k_{s,CO_2}) = \sum_{i=1}^4 (\text{NRMSD}_{CO_2} + \text{NRMSD}_{CH_4}) \quad (15)$$

222 where subscript  $i$  refers to experiment 1 to 4. Next using the flowchart of Babaei and Pan  
 223 (2016)[Fig.4],  $\mathbf{f}(k_{irr,MGH}, k_{irr,CGH}, k_{s,CH_4})$  is treated as  $F(\mathbf{u}_{candidate})$ . Instead of using any en-  
 224 semble surrogates, we use RBF to generate surrogates of the actual solver. The number of  
 225 function evaluations for Latin hypercube sampling ( $N_{LHS}$ ) and the total number of function  
 226 evaluations that calls the actual solver ( $N_{eval}$ ) are set equal to 40 and 100. Babaei and Pan  
 227 (2016) used  $N_{LHS} = 2n + 2$  (where  $n$  is the number of state variables, for our case  $n = 4$ ), and  
 228  $N_{eval} = 2.5N_{LHS}$  to successfully optimize a complex problem with four variables. Therefore, in  
 229 this study,  $N_{LHS} = 20$  and  $N_{eval} = 50$  are sufficient for optimization of objective function for  
 230 four parameters ( $\mathbf{u}$ ) using RBF. Furthermore, formulation of the objective function as above  
 231 considers all experiments conducted in this study and both measured inventory compounds.  
 232 The inventory  $CO_2$  and methane basically include all forms of the compound in the vessel (pure  
 233 (liquid or gaseous), aqueous, and hydrate), and can simply be calculated from the model as  
 234 follows:

$$CO_2^{inv.} = CO_{2(liquid)} + CO_{2(aqueous)} + CO_{2(hydrate)} \quad (16a)$$

$$CH_4^{inv.} = CH_{4(gas)} + CH_{4(aqueous)} + CH_{4(hydrate)} \quad (16b)$$

235 Note that methane cannot exist in liquid form in our experimental p/T conditions.

### 236 3.3 Model implementation

237 The model was implemented in COMSOL Multiphysics® using its *Reaction Engineering Mod-*  
238 *ule*. Two modeling setups, a batch and a reactor, were employed and coupled together. The  
239 inert components (gas-hydrates and sand) were simulated by the batch model and the mobile  
240 substances (water, CO<sub>2</sub> and methane) by the reactor model. The two modeling setups were  
241 linked together to ensure a correct mass and energy balance for the entire system. The chemical  
242 parameter values for hydrates and other components were taken from the literature or NIST  
243 Chemistry WebBook (Linstrom and Mallard, 2013), listed in Table 1.

244 To maintain the model numerical stability, any sudden change of the boundary conditions  
245 as well as shift of hydrate thermodynamics (from stable to instable and vice versa) at stability  
246 temperatures must be treated continuously. To that end, the CO<sub>2</sub> injection intervals in model  
247 were smoothed using a second derivative smoothing technique (COMSOL 4.3, 2013; Vermolen  
248 et al., 2009). A rigorous method was also applied for the definition of the local reaction rates  
249 (Section 3.1.3) to ensure a smooth transition of hydrate reaction rates from stable towards  
250 unstable conditions.

251 The COMSOL code is converted to function  $\mathbf{f}(k_{irr,MGH}, k_{irr,CGH}, k_s, CH_4$  with state variables  
252 as inputs and via COMSOL-MATLAB LiveLink™, optimization is carried out in MATLAB  
253 treating COMSOL as a black-box. We use MATSuMoTo toolbox in MATLAB to call RBF to  
254 construct surrogate model of COMSOL function (Müller and Piché, 2011; Müller, 2014) and  
255 speed up the optimization process.

### 256 3.4 Simulated scenarios

257 Four scenarios were simulated at the following pressure-temperature conditions where the ex-  
258 perimental data are available (Deusner et al., 2012):

- 259 • experiment 1: 13 MPa/2 °C
- 260 • experiment 2: 13 MPa/8 °C
- 261 • experiment 3: 13 MPa/10 °C
- 262 • experiment 4: 8 MPa/8 °C

263 The phase diagram in Fig. 1 illustrates the experimental conditions with respect to the  
264 thermodynamic stability regimes of CH<sub>4</sub>- and CO<sub>2</sub>-hydrate. The experiments were performed  
265 in a pressure vessel of 38 cm length, 8 cm cross section diameter, 18 mm casing thickness, with  
266 inlet (and outlet) of 13 mm diameter (Deusner et al., 2012).

267 The simulation developed to calibrate four experiments described above models a reactor  
268 with nearly two liters volume in which 95 °C CO<sub>2</sub> was injected during multiple intervals separated  
269 with periods of equilibrium.

## 270 4 Results and Discussion

### 271 4.1 Modeling results

272 In the present study, the major modeling results of interest are the temporal changes of (1) the  
273 reactor's average temperature, (2) the overall methane and CO<sub>2</sub> inventory, (3) the amount of  
274 methane- and CO<sub>2</sub>- hydrate, and (4) the overall system thermal conductivity (Figs. 3 to 6).

275 In the experiments, only the total amount of inventory methane and CO<sub>2</sub> (including all pure,  
276 dissolved or hydrate phases) was calculated using outlet and inlet volume balancing. Therefore,  
277 the primary aim was to obtain a proper fit first with the methane inventory data and then  
278 with the CO<sub>2</sub> inventory data, and then use the model to predict the fluctuations of temperature  
279 and gas-hydrate in the system. Since it was very difficult to directly record temperature values  
280 or determine the amount of gas-hydrates inside the pressure vessel, the use of model (after  
281 constraining the unknown parameters) helped to calculate these quantities that otherwise were  
282 unobtainable by means of laboratory equipments.

283 It is easy to approximately locate the start and the duration of injection intervals in Figs. 3  
284 to 6 where abrupt temperature changes occurs. The system's highest temperatures are gen-  
285 erally observed during the injection times when the average temperature of the system raised  
286 due to the entry of 95°C CO<sub>2</sub>. In all experiments, the majority of methane-hydrate dissociation  
287 occurred during the injection intervals when the system's temperature increased above the hy-  
288 drate stability temperature. Hence, the quicker the system reached or the longer it stayed at  
289 hydrate instability conditions, a higher amount of hydrate dissociation was obtained. In con-  
290 trast, the accumulation or precipitation of hydrate mainly occurred during equilibration periods  
291 after the system lost heat to the surroundings. Further details and distinguishing features for

292 every modeling scenario are separately addressed in the following sections.

#### 293 4.1.1 First scenario: 13 MPa/2 °C

294 The first experiment was performed at the lowest temperature leading to the lowest amount of  
295 methane-hydrate dissociation and the highest amount of CO<sub>2</sub> accumulation. The experiment  
296 time was about 44 hours in which the CO<sub>2</sub> was injected in four separate intervals. The maximum  
297 temperature reached only 285 K and was mainly achieved at the peak of injection intervals. Due  
298 to very low ambient temperature and high vessel pressure, the system hydrates were exposed to  
299 instability conditions only for a very short time. Most of the CO<sub>2</sub> was, therefore, speculated to  
300 deposit in the vessel as CO<sub>2</sub>-hydrate with excess pore water. The modeling results also confirmed  
301 the accumulation of CO<sub>2</sub>-hydrate in the system. The qualitative model reproduction of the  
302 experiment data of the CO<sub>2</sub> inventory supports this hypothesis and also suggests a homogeneous  
303 retention of the injected CO<sub>2</sub> in the vessel (Fig. 3).

304 The long equilibration periods between the injection intervals allowed CO<sub>2</sub> to slowly form  
305 CO<sub>2</sub>-hydrate and increased its retention yield. **The model predicted the formation of nearly**  
306 **3 mol CO<sub>2</sub>-hydrate inside the vessel while the methane-hydrate dissociation was predicted to**  
307 **be less than 0.1 mol.** A substantial formation of CO<sub>2</sub>-hydrate with the excess pore water was  
308 confirmed and was speculated as the main reason preventing rapid growth of preferential flow  
309 paths in this scenario.

#### 310 4.1.2 Second scenario: 13 MPa/8 °C

311 In comparison to the first experiment, the second experiment was done at a higher ambient  
312 temperature and therefore a significantly higher amount of methane-hydrate dissociation was  
313 observed (Fig. 4). While the length of experiment was marginally longer than the first experi-  
314 ment (about 45.5 hours), a higher amount of CO<sub>2</sub> was injected through five intervals (25% more  
315 CO<sub>2</sub> was injected in comparison to the first experiment). The amount of heat transferred to the  
316 vessel was therefore higher but this was not the only feature contributing to a higher amount  
317 of methane-hydrate dissociation. In this scenario, the system was exposed to the hydrate insta-  
318 bility conditions for a longer time thereby increasing the methane yield. Evidently, the small  
319 temperature difference between the experiment's initial condition and the hydrates instability  
320 zone derived the system to gas-hydrates instability conditions faster and led to the dissociation

321 of a larger amount of methane-hydrate (the second highest amongst all experiments). The CO<sub>2</sub>  
322 inventory was overestimated by the model. This suggests that the injected CO<sub>2</sub> was possibly  
323 conveyed through preferential flow paths that were created due to methane-hydrate dissocia-  
324 tion. Other factors such as consecutive injections, and a short equilibration time between the  
325 injection intervals, could also have enhanced the progression of the preferential flow paths in  
326 this experiment.

#### 327 4.1.3 Third scenario: 13 MPa/10 °C

328 The third experiment was done at the highest ambient temperature during which the CO<sub>2</sub>-  
329 hydrate was subjected to instability conditions for the entire duration of the experiment and  
330 therefore never formed. The modeled CO<sub>2</sub> inventory curves deviated even more from the ex-  
331 perimental data indicating once again the development of preferential flow paths prohibiting a  
332 spread of CO<sub>2</sub> into the reactor volume. Comparing the results with the previous scenarios, it  
333 is speculated that the development of preferential flow paths are even stronger and that the  
334 formation of such pathways can be a function of ambient system temperature. Modeling results  
335 predicted a slightly higher dissociation of methane-hydrate than the second experiment while in  
336 the reality it was lower (Fig. 5). It is speculated that in the absence of CO<sub>2</sub>-hydrate formation,  
337 the injected CO<sub>2</sub> at later stages followed the formerly generated pathways and discharged faster  
338 from the outlet. However, this was not the case for the second scenario where the slight forma-  
339 tion of CO<sub>2</sub>-hydrate during the equilibrium intervals might have plugged the previously formed  
340 pathways, forcing the injected CO<sub>2</sub> in the following stages to spread into the regions with high  
341 methane-hydrate concentration.

342 The modeling of this scenario revealed that the strongly developed and hydraulically con-  
343 nected preferential flow paths dramatically disturbed the uniform distribution of the heat that  
344 was introduced via the injection of supercritical CO<sub>2</sub>. Therefore, the interactions between the  
345 injected CO<sub>2</sub> with the remaining methane-hydrate in the vessel was limited. Most of the heat at  
346 later injection intervals was, thus, expelled from the system and, despite the higher experimental  
347 ambient temperature, a lower rate of methane-hydrate dissociation was achieved.

348 The results show a clear dissimilarity between modeled and experimental data since the  
349 beginning and particularly after the consecutive first and second injection intervals. The quick  
350 progression of the preferential paths in this scenario may thus not only be related to the absence

351 of CO<sub>2</sub>-hydrate formation but also may be favored by the consecutive injections at the beginning  
352 of the experiment. The total duration of this experiment was about 77 hours, the longest amongst  
353 all.

#### 354 4.1.4 Forth scenario: 8 MPa/8 °C

355 The fourth experiment (Fig. 6) was performed at a lower pressure compared to previous experi-  
356 ments. The ambient temperature as shown in Fig. 1 was slightly below the stability temperatures  
357 of both CO<sub>2</sub>- and methane-hydrate and equal to that in the second scenario. The system thus  
358 easily reached hydrate instability conditions during the CO<sub>2</sub> injection intervals. The highest  
359 amount of methane dissociation was achieved in this experiment given its total duration was  
360 longer (about 50% longer) than the second experiment. The formation of preferential flow paths  
361 is evident as a result of CO<sub>2</sub> inventory mismatch. The quick progress of preferential flow paths  
362 after the consecutive injections of CO<sub>2</sub> at the second and third intervals is visible. As for the  
363 second experiment the formation of CO<sub>2</sub>-hydrate favored the distribution of the injected CO<sub>2</sub>  
364 and enhanced the overall methane-hydrate dissociation in comparison with the third experiment.  
365 The experiment took roughly 71 hours to complete.

## 366 4.2 Estimated kinetic parameters

367 Most of the parameter values were taken from the literature, or calculated by SUGAR toolbox  
368 (Kossel et al., 2015) in close approximation with the previously reported values (see Table 1).  
369 The only unknown parameters that often vary between different systems were  $k_{irr,MGH}$ ,  $k_{irr,CGH}$   
370 ,  $k_{s,CH_4}$ , and  $k_{s,CO_2}$ . Using the above described optimization technique we obtained the fol-  
371 lowing values for these parameters  $k_{irr,MGH} = 0.02(\text{mol.m}^{-3}\text{s}^{-1})$ ,  $k_{irr,CGH} = 0.03(\text{mol.m}^{-3}\text{s}^{-1})$ ,  
372  $k_{s,CH_4} = 4 \times 10^{-5}(\text{s}^{-1})$ , and  $k_{s,CO_2} = 1 \times 10^{-5}(\text{s}^{-1})$ . This values are in agreement with previously  
373 reported values. For instance, the values of  $k_{s,CH_4}$  and  $k_{s,CO_2}$  are in the same range of values  
374 reported in Noyes et al. (1996) for first-order gas-exchange rate constant. The estimated values  
375 for parameters describing hydrates dissociation at absolute instability conditions,  $k_{irr,MGH}$  and  
376  $k_{irr,CGH}$ , were about two orders of magnitude lower than the value reported in Jerbi et al. (2010)  
377 for CO<sub>2</sub> dissociation. However, Jerbi et al. (2010) performed the experiments in a semi-batch  
378 stirred tank reactor at stirring velocity of 450 rpm. A simple comparison between the two sys-  
379 tems (pressure vessel and stirred-tank reactor) shows that it is reasonable to obtain significantly



380 lower dissociation rates in a pressure vessel.

381 We were able to obtain a convenient fit to methane inventory data for all the scenarios except  
382 the third one performed at 13 MPa/10 °C. The fact that neither the model results for methane  
383 inventory nor the results for CO<sub>2</sub> inventory of the third scenario were found to reasonably fit to  
384 the experimental data (Fig. 5) suggests that the underlying processes in this experiment were  
385 too complicated to be described by the modeling approach presented. It is therefore difficult  
386 from this approach to correlate the rate of methane-hydrate dissociation in the third experiment  
387 with those in other scenarios. On the contrary, the model results did not fit properly to the CO<sub>2</sub>  
388 inventory data at all. This might be mainly due to the development of preferential flow paths  
389 in the system causing the CO<sub>2</sub> to poorly spread in the reactor volume and to leave the reactor  
390 early. Since the current model assumptions are based on perfect mixing, any deviation of model  
391 results from the CO<sub>2</sub> inventory data can be linked to the occurrence of preferential flow paths  
392 and the heterogeneous transport of CO<sub>2</sub> inside the vessel.

393 The aim was not, however, to obtain a perfect fit to each experiment with any combination of  
394 the values, but to find for each of these parameters a constant value to which a reasonable fit can  
395 be achieved to all the scenarios. It is worth noting that most of the parameters in reality might  
396 be a function of temperature, pressure and salinity. Since pressure was kept nearly constant in  
397 the vessel and the temperature of the system fluctuated within a narrow band, the majority of  
398 chemical properties including the estimated effective rates were assumed constant.

### 399 4.3 Dissolution rate of methane and carbon dioxide in water

400 A significant sensitivity of the model to the dissolution rates of methane and CO<sub>2</sub> in water was  
401 found during the model analysis. It was displayed that not only the final aqueous concentrations,  
402  $c_{cte,CH_4}$  and  $c_{cte,CO_2}$  (calculated from SUGAR toolbox (Kossel et al., 2015) and listed in Table 1),  
403 but also the exchange rate constants between water and gas,  $k_{s,CH_4}$  and  $k_{s,CO_2}$ , are important  
404 for the dissociation/formation of the hydrate at the beginning of the experiments and after  
405 the injection intervals. Numerical stability of the model was found to be very sensitive to the  
406 values of these parameters. These parameters might be less influential at field-scale than in  
407 the experiments due to the comparatively larger computation time-scales or larger size of the  
408 domain.

#### 409 4.4 The relation between carbon dioxide retention and methane release

410 The present findings speculate that the differences between modeling and experimental results  
411 are associated with the presence of flow heterogeneities and their relative growth inside the  
412 vessel. Since model predictions are based on perfect mixing assumptions, the differences between  
413 model predictions and experimental data in CO<sub>2</sub> inventory curves (Figs. 4 and 6) indicate that  
414 the injected CO<sub>2</sub> bypassed the majority of the vessel contents in all scenarios except the first  
415 one. This, however, only hindered the methane-hydrate dissociations in the third experiment,  
416 suggesting that in both, the second and fourth scenarios the injected CO<sub>2</sub> still managed to  
417 deliver its heat to the vessel contents.

418 The only major difference between other scenarios and the third scenario is the formation  
419 of CO<sub>2</sub>-hydrate, which appears to affect positively the dissociation of methane-hydrate in the  
420 second and the fourth scenarios. The reason may be related to the formation of solidified CO<sub>2</sub>-  
421 hydrate clogging up the previously formed flow pathways, thereby forcing the upcoming CO<sub>2</sub>  
422 to choose a different pathway. Alternatively, the lower enthalpy of formation of CO<sub>2</sub>-hydrate in  
423 comparison to methane-hydrate may have thermodynamically favored methane-hydrate disso-  
424 ciation. Either way, it appears that at p/T conditions closer to the methane-hydrate instability  
425 zone, the retention of CO<sub>2</sub> catalyzes the methane-hydrate dissociation. This might have the  
426 following practical implications for CO<sub>2</sub> injection into hydrate reservoirs. First, the tempera-  
427 ture of the injected CO<sub>2</sub> can be adjusted in order to avoid the reservoir temperatures at which  
428 CH<sub>4</sub>-hydrate is stable and CO<sub>2</sub>-hydrate is unstable (at p/T conditions similar to the third sce-  
429 nario). Secondly, altering the reservoir conditions to the p/T conditions at which CH<sub>4</sub>-hydrate  
430 is unstable and CO<sub>2</sub>-hydrate is stable might increase both CO<sub>2</sub> retention yield and CH<sub>4</sub>-hydrate  
431 dissociation. This might be only obtainable by combining the two techniques of depressurization  
432 and thermal stimulation together. Accordingly, it might be safe to say that injection of CO<sub>2</sub> into  
433 the gas-hydrate reservoirs at p/T conditions similar to the third scenario is not economically  
434 and environmentally favorable.

#### 435 4.5 Guidelines for field-scale modeling

436 The dissociation of hydrate was not entirely related to the amount of heat that was introduced  
437 to the system but to the quality of heat distribution, information that is difficult to quantify em-  
438 pirically. The comparison between an ideally mixed model and experimental data allowed us to

439 interpret the system behavior in each case based on the discrepancies observed. Methane-hydrate  
440 dissociation yield is likely related to the relative combination of several factors that cannot be  
441 imposed externally, such as reservoir temperature, pressure, salinity, structural heterogeneities,  
442 composition of sand layers, or the spatial distribution of these quantities. In turn, several factors  
443 can be regulated during the production from gas-hydrate deposits which were discovered to have  
444 a noteworthy influence on the final results. These include temperature of superheated CO<sub>2</sub>, the  
445 equilibration periods between injection intervals, and the injection strategy. The succession of  
446 injection intervals was shown detrimental to the whole process due to bolstering the preferential  
447 flow paths and thus decreasing the quality of heat expansion. The mismatches between model  
448 and experiments were mostly observed after the consecutive injections. The longer the equili-  
449 bration intervals, the lesser was the extension of preferential pathways through the vessel. Low  
450 injection rates of CO<sub>2</sub> were found to benefit the CO<sub>2</sub> retention process through homogenizing  
451 the distribution of CO<sub>2</sub>, allowing it to disperse further into the depth of hydrate deposit while  
452 preventing the restoration of preferential flow paths. A similar finding has been recommended  
453 by [White et al. \(2011\)](#). It is also suspected that the formation of CO<sub>2</sub>-hydrate not only im-  
454 proved the quality of CO<sub>2</sub> retention but also enhanced the overall methane-hydrate dissociation.  
455 Therefore, the method at p/T conditions between the two hydrates stability curves (at condi-  
456 tions similar to the third experiment) was shown highly ineffective. However, more data are  
457 needed to prove that the CO<sub>2</sub>-CH<sub>4</sub>-hydrate conversion must be avoided at such p/T conditions  
458 by performing more experiments at such conditions.

459 In addition, it was shown that the pore-scale heterogeneities that are typically ignored at  
460 field-scale models can immensely affect the simulation results. Since the inclusion of such small-  
461 scales effects into reservoir models is computationally very elaborate, the urge of upscaled models  
462 which are able to estimate the small-scale (cm to meters) dynamics in the presence of hetero-  
463 geneities as a function of system pressure and temperature is noted. These models can be either  
464 empirical or analytic.

#### 465 4.6 Model predictability and limitations

466 It was shown that the model performs better at low temperatures and high pressures deep  
467 inside the hydrate stability zone (at conditions similar to the first experiment). However, the  
468 predictability of model reduced at higher temperatures, closer to hydrate instability zone (at

469 conditions similar to the third experiment). The analysis of results shows that the presented  
470 model was able to forecast the behavior of a (semi-)homogenized system. A similar findings  
471 was noted by the Ignik Sikumi field trial (Schoderbek et al., 2013). The deviations between  
472 modeling results and experiments occurred when preferential flow paths played a major role on  
473 the transport of substances, and when the system become extremely heterogeneous.

## 474 5 Conclusions and Implications

475 We presented here the results of a kinetically-focused simulation which is used to explain the ex-  
476 perimental results reported in Deusner et al. (2012) without extra complexities of fully spatially-  
477 resolved, computationally-expensive fluid dynamics simulations. Unlike most of the studies in  
478 this field in which the focus has been given to the fluid dynamics and transport effects and as  
479 a result reaction kinetics were oversimplified, in this study a detailed definition of kinetics was  
480 employed. The transport phenomena, however, were simplified to a basic mass and energy bal-  
481 ance for a representative elementary volume (2 liters) which is equal or smaller than the typical  
482 size of a grid block in continuum field-scale models. This study demonstrates the significance of  
483 reaction kinetics on the extraction of natural gas through the injection and exchange of CO<sub>2</sub> with  
484 methane in gas-hydrates. The details of kinetics are therefore shown to be too significant to be  
485 easily discarded despite the fact that such simplifications are commonly observed in field-scale  
486 models. Furthermore, it is noted that an equal emphasis should be given to the details of small-  
487 scale heterogeneities in reservoir simulators in order to correctly model hydrate exploitation at  
488 field-scale. To avoid excessive computational demands of high-resolution models at field-scale  
489 while taking the effects of pore-scale heterogeneities into consideration, it is required to develop  
490 upscaled models that perform at small scales (cm to m). Such up-scaled models do not ex-  
491 plicitly solve all the transport mechanisms in details, but describe and encapsulate the overall  
492 impact of small-scale heterogeneities into a relatively accurate and computationally-inexpensive  
493 box-model. With the help of the model we estimated the values of key intrinsic parameters that  
494 are unknown, and are different depending on the experimental setup employed. These parame-  
495 ters are usually difficult to directly quantify from the experiments and as a result often over or  
496 underestimated.

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601 **Tables**

Table 1: Parameter values used in this study. Some of the parameter values are recalculated using SUGAR toolbox (Kossel et al., 2015) for the p/T conditions and the salinity of each scenario. For the rest of parameters the values from literature are taken as default.

Parameter (Unit dimension)	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Literature values
Heat capacity of CH <sub>4</sub> -hydrate ( $Jmol^{-1}K^{-1}$ )	251.18	268	275.8	268	258 <sup>a</sup>
Heat capacity of water ( $Jmol^{-1}K^{-1}$ )	73.8	73.91	73.95	74.16	75.4 <sup>b</sup>
Heat capacity of CO <sub>2</sub> -hydrate ( $Jmol^{-1}K^{-1}$ )	307.77	328.38	337.95	328.38	
Heat capacity of methane ( $Jmol^{-1}K^{-1}$ )	59.5	57.21	56.53	47.69	34.8 <sup>c</sup>
Heat capacity of CO <sub>2</sub> ( $Jmol^{-1}K^{-1}$ )	92.97	95.71	96.77	106.62	103 <sup>d</sup>
Heat capacity of sand (Quartz) ( $Jkg^{-1}K^{-1}$ )					730 <sup>d</sup>
Heat transfer coefficient of the steel jacket ( $Wm^{-1}K^{-1}$ )					16 <sup>e</sup>
Thermal conductivity of water ( $Wm^{-1}K^{-1}$ )	.575	.585	.588	.583	0.58 <sup>f</sup>
Thermal conductivity of CO <sub>2</sub> ( $Wm^{-1}K^{-1}$ )	.123	.116	.114	.108	0.1 <sup>g</sup>
Thermal conductivity of CH <sub>4</sub> ( $Wm^{-1}K^{-1}$ )	.05	.05	.05	.042	0.051 <sup>h</sup>
Thermal conductivity of CH <sub>4</sub> -hydrate ( $Wm^{-1}K^{-1}$ )					0.62 <sup>h</sup>
Thermal conductivity of CO <sub>2</sub> -hydrate ( $Wm^{-1}K^{-1}$ )					0.49 <sup>d</sup>
Thermal conductivity of water-saturated sand ( $Wm^{-1}K^{-1}$ )					3.3 <sup>i</sup>
CH <sub>4</sub> -hydrate enthalpy of dissociation ( $kJmol^{-1}$ )					54.2 <sup>o</sup>
CO <sub>2</sub> -hydrate enthalpy of dissociation ( $kJmol^{-1}$ )					82 <sup>j</sup>
Activation energy of CH <sub>4</sub> -hydrate dissociation ( $kJmol^{-1}$ )					81 <sup>j</sup>
Activation energy of CH <sub>4</sub> -hydrate formation ( $kJmol^{-1}$ )					20.6 <sup>k</sup>
Activation energy of CO <sub>2</sub> -hydrate dissociation ( $kJmol^{-1}$ )					102 <sup>j</sup>
Activation energy of CO <sub>2</sub> -hydrate formation ( $kJmol^{-1}$ )					20 <sup>l</sup>
Dissolution kinetic constant of CH <sub>4</sub> -hydrate ( $mol\ m^{-2}\ s^{-1}\ Pa^{-1}$ )					$3.6 \times 10^4$ <sup>m</sup>
Formation kinetic constant of CH <sub>4</sub> -hydrate ( $mol\ m^{-2}\ s^{-1}\ Pa^{-1}$ )					0.6 <sup>n</sup>
Dissolution kinetic constant of CO <sub>2</sub> -hydrate ( $mol\ m^{-2}\ s^{-1}\ Pa^{-1}$ )					$1.83 \times 10^8$ <sup>j</sup>
Formation kinetic constant of CO <sub>2</sub> -hydrate ( $mol\ m^{-2}\ s^{-1}\ Pa^{-1}$ )					$5 \times 10^{-3}$ <sup>o</sup>
Equilibrium concentration of CH <sub>4</sub> , $c_{cte,CH4}$ ( $mol\ m^{-3}$ )	156.36	139.34	134.5	102.6	
Equilibrium concentration of CH <sub>4</sub> -hydrate, $c_{cte,MGH}$ ( $mol\ m^{-3}$ )	58.49	84.33	95.53	85.51	
Equilibrium concentration of CO <sub>2</sub> , $c_{cte,CO2}$ ( $mol\ m^{-3}$ )	1884.05	1695.93	1642.09	1625.52	
Equilibrium concentration of CO <sub>2</sub> -hydrate, $c_{cte,CGH}$ ( $mol\ m^{-3}$ )	909.1	1376.34	1617.89	1386.51	

<sup>a</sup>Handa (1986)

<sup>b</sup>Koh et al. (2011)

<sup>c</sup>Waite et al. (2009) at 260K

<sup>d</sup>Jung et al. (2010)

<sup>e</sup>Vessel manual

<sup>f</sup>Waite et al. (2009)

<sup>g</sup>NIST Chemistry WebBook (Linstrom and Mallard, 2013)

<sup>h</sup>Waite et al. (2007)

<sup>i</sup>Tarnawski et al. (2011)

<sup>j</sup>Clarke and Bishnoi (2004)

<sup>k</sup>Freer et al. (2001)

<sup>l</sup>Estimated

<sup>m</sup>Clarke and Bishnoi (2001); Kim et al. (1987)

<sup>n</sup>Englezos et al. (1987)

<sup>o</sup>Clarke and Bishnoi (2005)



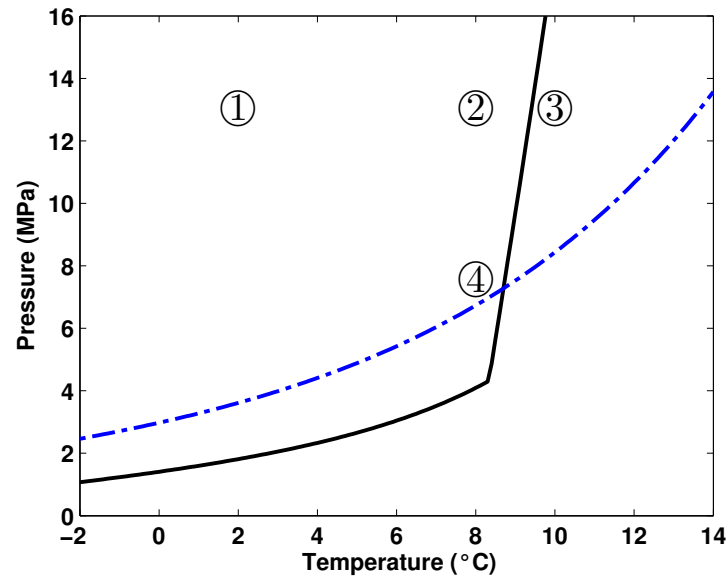


Figure 1: Stability curves for methane-hydrate (blue dotted line) and  $\text{CO}_2$ -hydrate (black solid line) in respect to system pressure and temperature. At high pressures and low temperatures inside the stability zone hydrate dissolves/forms according to Reactions 8a and 8b. Outside the hydrate stability zones at high temperatures and low pressures hydrate only dissociates (Reactions 9a and 9b). The encircled numbers indicate the pressure and temperature conditions at which the experiments were performed.

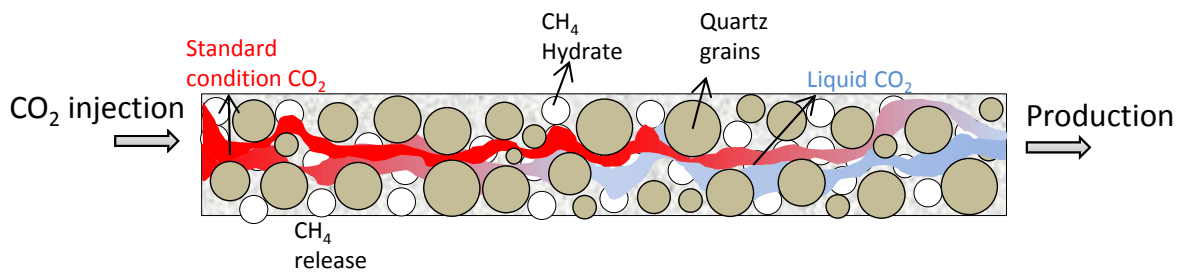


Figure 2: The schematic diagram of the processes occurring during supercritical  $\text{CO}_2$  injection into the pressure vessel containing  $\text{CH}_4$ -hydrate and sand.

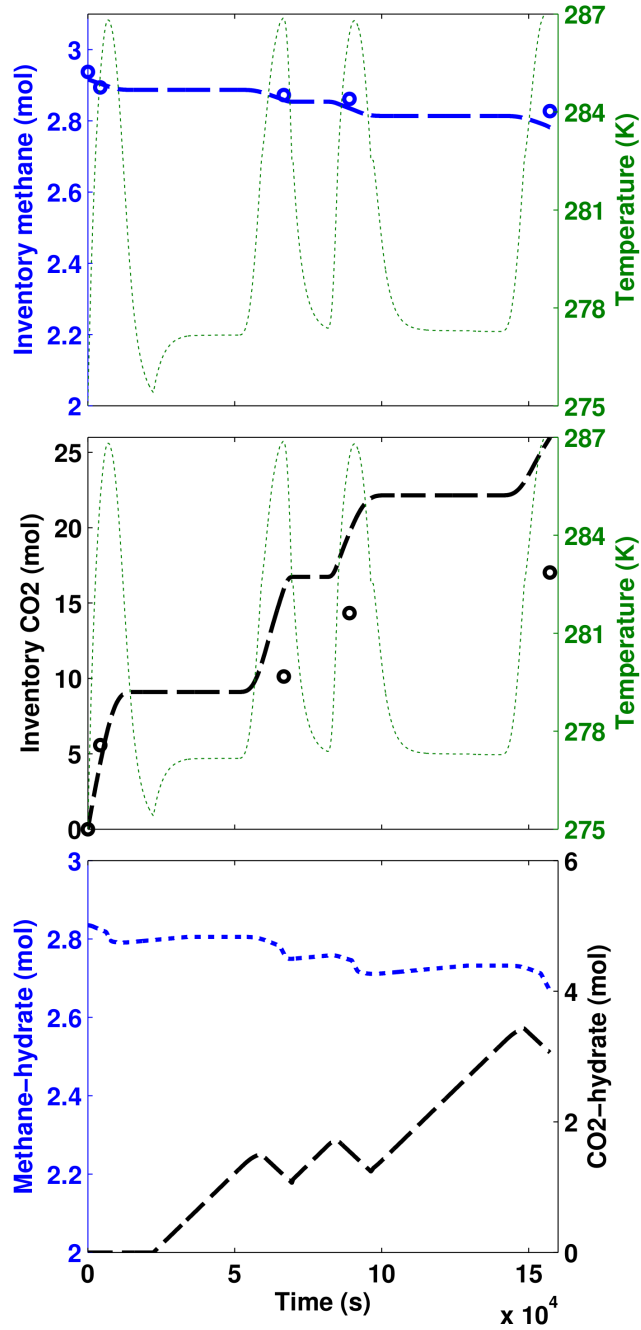


Figure 3: The modeling results of first scenario are shown by dashed lines and open dots are the reported experimental data for the p/T conditions of 13MPa and 2°C.

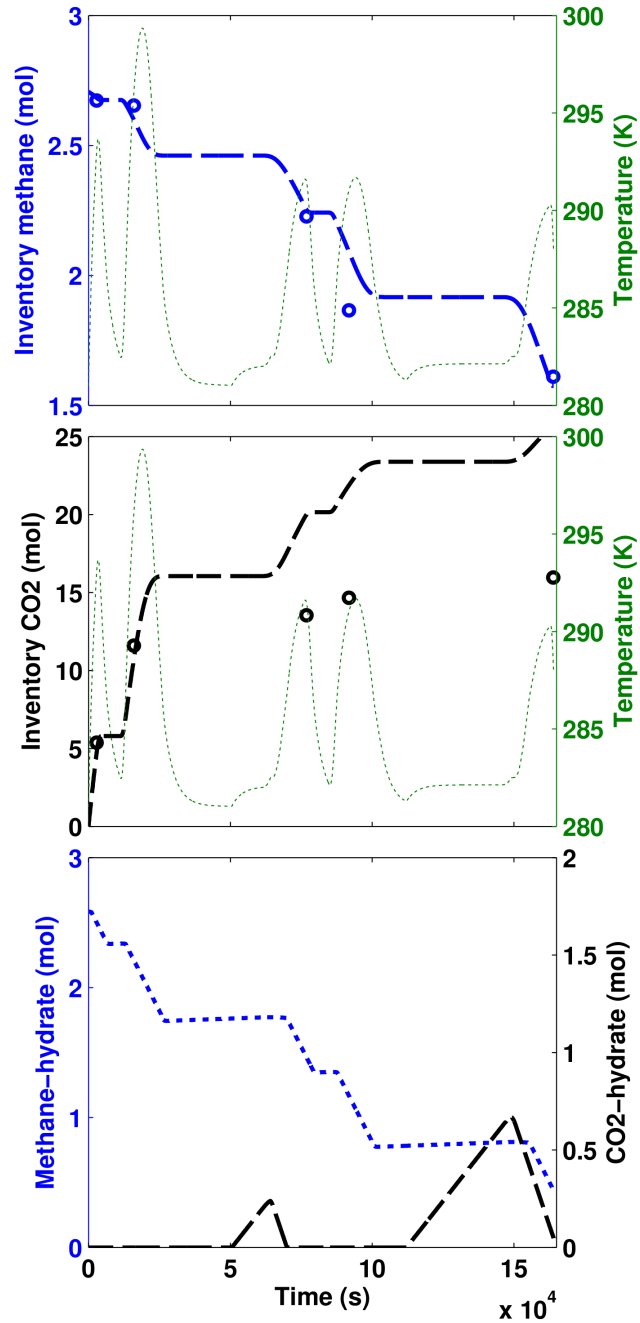


Figure 4: The modeling results of second scenario are shown by dashed lines and open dots are the reported experimental data for the p/T conditions of 13MPa and 8°C.

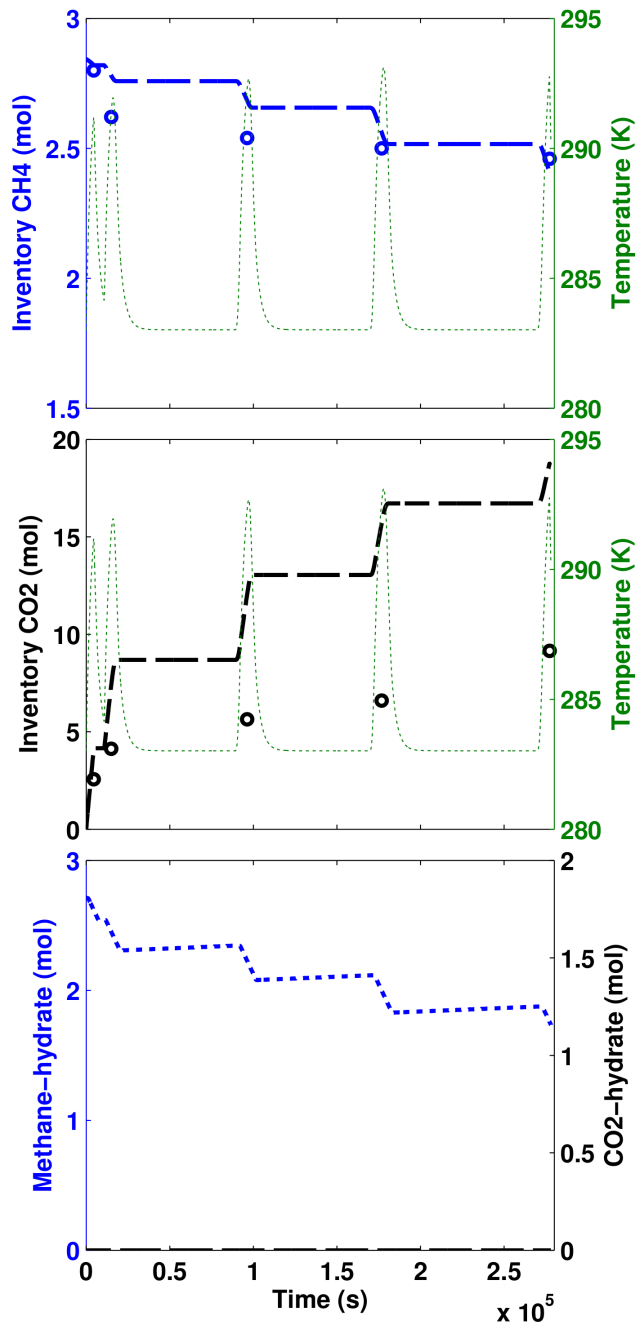


Figure 5: The modeling results of third scenario are shown by dashed lines and open dots are the reported experimental data for the p/T conditions of 13MPa and 10°C.

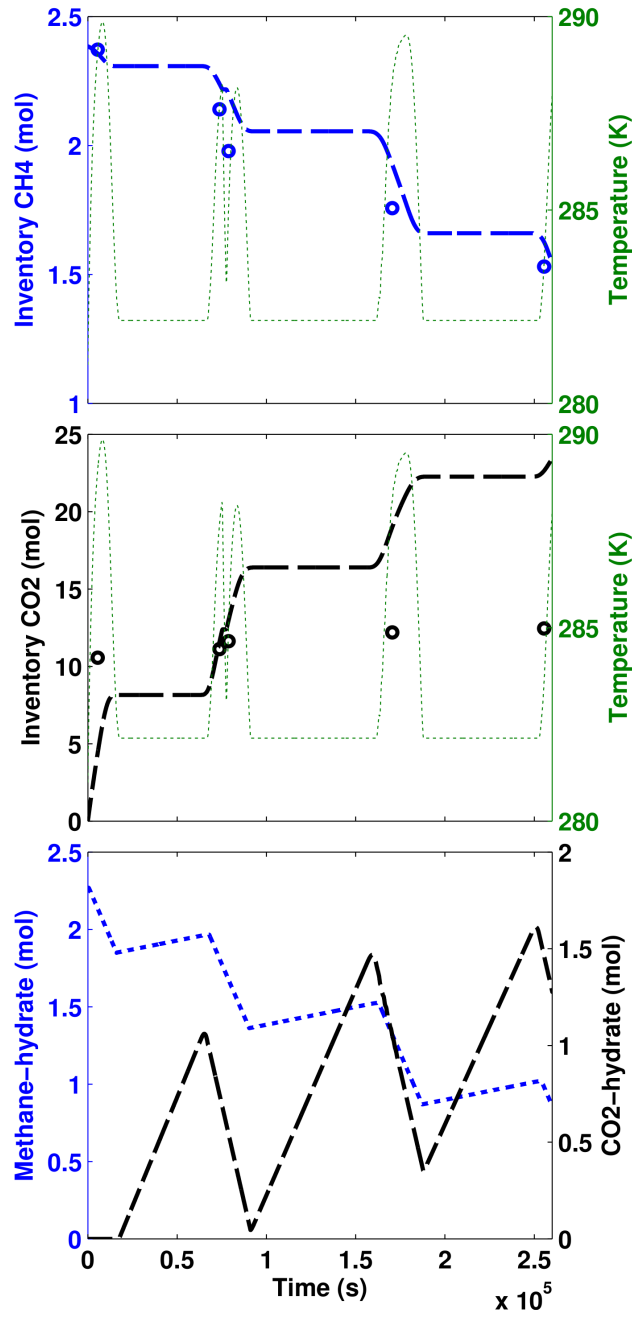


Figure 6: The modeling results of forth scenario are shown by dashed lines and open dots are the reported experimental data for the p/T conditions of 8MPa and 8°C.