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An experimental system and procedure of unsteady-state relative permeability test for gas hydrate-bearing sediments

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3 **An Experimental System and Procedure of Unsteady-State**

4 **Relative Permeability Test for Gas Hydrate-Bearing**

5 **Sediments**

6

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19 **Abstract**

20 Reliable estimations of the relative permeability of gas and water in
21 hydrate-bearing sediments (HBS) and the dependency of the relative
22 permeability on hydrate saturation are critical to predict the productivity of a
23 hydrate reservoir. Yet, this remains poorly estimated owing to lack of
24 experimental data associated with difficulties in conducting multiphase flow
25 experiments in HBS. Recognizing the experimental challenges, this study
26 intends to develop and validate a new experimental system and procedure of
27 unsteady-state relative permeability test that can generate reliable and
28 reproducible flow measurements in HBS. Gas hydrate is considered as a part
29 of solid matrix in the sediment, so one of the challenges is to maintain a
30 constant hydrate saturation, which is achieved in this experimental study
31 using tight pressure-temperature (P-T) control near the hydrate stability
32 boundary. The measured differential pressure across the specimen,
33 methane injection flow rate, and volume of displaced brine are used to
34 calculate the relative permeability by adopting a conventional Buckley-
35 Leverett theory-based interpretation method. Residual brine saturation
36 calculated for the hydrate-bearing specimen is higher than that of hydrate-
37 free specimen, presumably due to decrease in pore size, increase in
38 heterogeneity of solid matrix, and increase in size distribution of solid matrix
39 and pore in the presence of hydrates. Further studies are necessary to
40 represent the results of the unsteady-state flow experiment in HBS with a
41 gas hydrate-dependent relative permeability model.

42

43 **Keywords:**

44 Unsteady-state relative permeability test, hydrate-bearing sediments,
45 methane-brine relative permeability, residual saturation

46

47 **1. Introduction**

48 The volume of natural gas trapped in gas hydrates is reported to be
49 enormous (Collett et al., 2009), which makes natural gas hydrates a potential
50 energy resource in the future (Boswell, 2009; Makogon et al., 2007). Several
51 onshore and offshore gas production tests have been conducted, e.g., Alaska
52 North Slope, Mackenzie Delta, Nankai Trough, Gulf of Mexico, South China
53 Sea, and so on, to examine the viability of gas production from hydrate
54 reservoirs (Boswell et al., 2017; Dallimore et al., 2005; Li et al., 2018;
55 Schoderbek et al., 2013; Yamamoto, 2013). To date the field tests are
56 limited to short-term gas production from hydrate-bearing reservoirs.
57 Numerical simulations that analyze multiphase flow through hydrate
58 reservoirs remain a practical tool to evaluate the long-term production
59 potential. Permeability of different fluid phases in hydrate reservoir is a
60 fundamental input for such long-term numerical simulations (Anderson et al.,
61 2011; Moridis et al., 2011; Myshakin et al., 2019; White et al., 2011).

62 Permeability of hydrate-bearing sediments (HBS) has two aspects. The
63 first is the single-phase permeability, often called effective permeability with
64 the presence of hydrates. Such permeability pertains to a measure of

absolute permeability change relative to the amount of hydrate contained in lab-made or natural HBS, and its experimental measurement has been reported by many studies (Delli and Grozic, 2014; Konno et al., 2015b; Kumar et al., 2010; Liang et al., 2011; Sakamoto et al., 2004; Seol et al., 2006; Yoneda et al., 2019). The second is the relative permeability of mobile phases (gas and water) that describes the competitive flow of both phases in HBS. Experimental measurements of such relative permeability have been reported by only a few studies (Ahn et al., 2005; Jaiswal, 2004; Johnson et al., 2011). However, some information was missing from these studies (e.g. detailed description of sample preparation, experimental systems, conditions, and/or procedures) that can be referred to for similar succeeding studies. The primary reason for the scarcity of gas-water relative permeability tests on HBS involves technical difficulties in limiting thermodynamic instability of gas hydrate in HBS during the multiphase flow (Johnson et al., 2011). The experimental difficulties have also led researchers to predict gas-water relative permeabilities in HBS using computational approaches (Mahabadi et al., 2016; Mahabadi and Jang, 2014; Singh et al., 2019; Singh et al., 2018), but the predicted results have not been vetted against robust laboratory measurements. Therefore, the development of an experimental setup, as well as an experimental procedure, is critical to obtain reliable and reproducible measurements that can be utilized to develop and validate relative permeability relationships in the presence of hydrates and to estimate relevant parameters for numerical

88 simulations of gas production from hydrate reservoirs.

89 This study first presents experimental challenges occurring during the
90 relative permeability test on HBS. Experimental systems and procedures to
91 mitigate the challenges and to conduct unsteady-state drainage relative
92 permeability tests on HBS are then introduced. Thereafter, validation of the
93 developed experimental methodology is performed, as well as the analysis of
94 resulting relative permeabilities of methane and brine in the presence of gas
95 hydrate. Some key research aspects, e.g., capillary heterogeneity that
96 possibly results from pore size reduction/redistribution in presence of
97 hydrate and thereby affects inferred relative permeability values, are
98 discussed in respect of future studies at the end.

99

100 **2. Experimental Challenges**

101 Experimental challenges faced in conventional multiphase flow
102 characterization of sediments become more complicated when gas hydrate
103 exists in the pores of the medium. The primary reason for the complication
104 is the dynamic change in thermodynamic equilibrium between gas hydrate
105 and mobile phases that can cause either hydrate formation or dissociation
106 upon applied pressure-temperature (P-T) condition which even changes to an
107 extent across the length of a sample. This leads to a change in gas hydrate
108 saturation in the pore space that alters the hydraulic characteristics of the
109 original HBS. In the following sections, the experimental challenges that
110 should be considered for reproducible relative permeability measurements of

111 HBS are addressed.

112

113 HBS Sample Preparation: Pressure cores retrieved from natural hydrate
114 reservoirs are generally preferred for physical property characterization of
115 HBS. However, there would be mechanical and P-T disturbances to the
116 pressure cores that are hardly avoidable during coring, transferring, storing,
117 and subsequent handling processes (Dai and Santamarina, 2014). In
118 addition, the rare and expensive retrieved cores may not be representative
119 for the whole reservoir considering large variability in lithofacies and
120 compositions. Laboratory synthesized cores can be an alternative to the
121 natural cores if they are adequately prepared under well-controlled P-T
122 conditions, with representative sediment composition, hydrate saturation,
123 and nature-like hydrate pore habit. The main challenge is to mimic the way
124 hydrates form in natural sediments typically featuring pore-filling gas
125 hydrate under excess-water conditions. A few sample preparation
126 procedures have been proposed to synthesize the HBS having pore-filling,
127 load-bearing, and/or patchy type hydrates under excess-water condition
128 (Choi et al., 2014; Katsuki et al., 2007; Lei et al., 2019; Priest et al., 2009;
129 Spangenberg et al., 2005; Yang et al., 2008).

130

131 Maintaining Hydrate Saturation/Measuring Gas and Liquid Saturations in
132 HBS: Mobile phases (gas and water) flow through the sediment matrix
133 (sediment particles and hydrates) either solely or jointly, and their

134 permeabilities need to be measured at each specific hydrate saturation so
135 that full relative permeability contours of the three-phase system, i.e.,
136 hydrate + gas + liquid, can be built by consolidating all the relative
137 permeability curves measured at different hydrate saturations (Seol and
138 Kneafsey, 2011). Hydrate saturation and pore habit in the sediment,
139 however, can vary depending on sediment characteristics (grain sizes,
140 mineralogy, degrees of compaction, etc.) and thermodynamic reactions of
141 hydrate, gas, and liquid under the applied experimental conditions, and
142 these variations can influence the permeabilities (Dai and Seol, 2014; Kumar
143 et al., 2010; Mahabadi et al., 2016; Mahabadi and Jang, 2014). Ideally,
144 permeability measurement should be conducted under a condition where the
145 three phases are thermodynamically stable, so that hydrate formation,
146 dissociation, and redistribution can be avoided. Experimental systems
147 should **1)** control P-T to keep hydrate disturbance as minimal as possible, **2)**
148 monitor P-T changes in real time to allow timely P-T adjustments, and **3)**
149 provide gas and liquid pre-saturated with each other to minimize molecular
150 exchange between the two mobile phases and prevent hydrate from
151 dissolving into liquid during permeability tests. In addition, to ensure the
152 maintenance of overall hydrate saturation in the sediment during
153 permeability tests, the systems should be able to detect the signs of extra
154 hydrate formation and dissociation manifested through changes in effluent
155 flow rates, so capabilities to measure such changes would be essential.

156 At a fixed hydrate saturation, the gas-liquid relative permeability is a

157 function of either gas or liquid saturation, and thus the mobile phase
158 saturations in the presence of hydrate need to be measured during the test
159 to derive the relative permeability relationship. To minimize possible errors
160 in calculating mobile phase saturations, it is preferred to measure the
161 volume of either mobile phase at the P-T condition applied to the test.

162

163 Maintaining Stable Back Pressure: Performing a relative permeability test
164 requires an experimental system capable of maintaining stable back
165 pressure. During the fluid flow, the pore pressure at the outlet face of a
166 specimen is controlled by maintaining the pressure at the end point of
167 downstream line (i.e., back pressure). In general, the pressure-valve-type
168 back pressure regulator (BPR) is used for the back pressure control (Ahn et
169 al., 2005; Jaiswal, 2004; Johnson et al., 2011), due to its advantages of no-
170 limit on fluid-flow-through capacity and smaller size over syringe pressure
171 pumps. However, in the gas-liquid relative permeability test on HBS, when
172 the pressurized gas flows into the BPR and the gas pressure maintained by
173 the BPR drops to atmospheric pressure at the pressure release point of BPR,
174 the volume expansion of gas occurs that causes a temperature drop due to
175 the Joule-Thompson effect. This can induce ice formation with concurrently
176 exiting mobile liquid. The ice formation can partially or completely clog flow
177 line ends and regulators, which leads to unstable back pressure control and
178 excessive fluctuations in line pressure and differential pressure (ΔP).
179 Therefore, a flow line should be designed to systematically limit excessive

180 gas volume expansion and preclude ice formation at the BPR for stable
181 control of pore pressure and quality data collections.

182

183 Prevention of Clogging in Flow Lines from Unintended Hydrate Formation:

184 Gas hydrate is known to form massive plugs in oil and gas pipelines, which
185 causes blockages and pressure buildup. This is considered as a major
186 operational hazard for the gas-oil industry (Deaton and Frost, 1946). The
187 same type of flow line clogging remains challenging in bench-scale hydrate
188 laboratory studies as well. The measurement of gas-liquid relative
189 permeability in HBS inevitably introduces gas-liquid interfaces in flow lines,
190 where hydrate can easily form to partially or completely clog the lines if the
191 P-T condition falls within the hydrate stability zone. Partial or complete
192 hydrate clogging of the lines can occur and interferes pressure transmission
193 through experimental system, leading to false readings of transducers (line
194 pressure, ΔP , and mass flow). The entire experimental system should,
195 therefore, be divided by sections in accordance with the order of
196 vulnerability to unintended hydrate formation, so that the individual sections
197 can be inspected in the order at the occurrence of signs of clogging. This
198 helps identify clogged spots with ease and remove them with minimal
199 disturbance on the whole system-wise flow regime and hydrate stability in
200 the specimen.

201

202 Prevention of Particle Loss from HBS Specimen: During the fluid flow, solids

203 in HBS specimen, including soil particles and hydrates, can migrate out of
204 the specimen. Such migration alters the pore network of HBS specimen and
205 can cause malfunctions in downstream regulators, transducers, and phase
206 separators, as well as clogging in downstream flow lines, which adversely
207 affects the quality of measured data for the permeability estimations.
208 Several factors, such as flow velocity (or drag force), fluid chemistry, fines
209 size (or weight), and pore throat size, should be carefully considered to
210 inhibit or mitigate particle moving (Han et al., 2020; Oyeneyin et al., 1995;
211 Sharma et al., 1992; Wan and Tokunaga, 2002). Preferably, to avoid the
212 particle loss from the specimen and the damages to critical test equipment,
213 direct preventive measures including filtration of migrating particles should
214 be incorporated into the test setup, either on specimen or downstream flow
215 lines depending on soil composition and fluid flow rates adopted during the
216 permeability tests.

217

218 **3. Relative Permeability Test Method**

219 **3.1. Overview**

220 There are two methods generally adopted for the relative permeability
221 measurement: steady-state and unsteady-state method. The steady-state
222 method adopts simultaneous injections of two or more immiscible fluids
223 through a specimen at a fixed injection ratio of the fluids until differential
224 pressure and fluid saturations across the core are equilibrated. The
225 equilibrated differential pressure and the volumetric injection rate of each

226 fluid are then used to calculate the relative permeability of the fluid at the
227 fluid saturation measured. This “steady-state equilibrium flow test” should
228 be repeated at different injection ratios of the fluids to form a relative
229 permeability curve of each fluid over the range of fluid saturation. The
230 steady-state method has advantages over the unsteady-state method, such
231 that the relative permeability calculation is easily made with the effective
232 permeability of each fluid calculated by a simple Darcy’s law at a given fluid
233 saturation, and it is generally considered reliable as it involves simultaneous
234 equilibrium of fluid flows rather than the displacement of one fluid by others,
235 so that the test results are rarely affected by viscous instability (Maini et al.,
236 1990; Peters, 2012). Disadvantages in the steady-state method include that
237 the equilibria of pressure and fluid saturation (or fluid flows) at each injection
238 ratio take a prolonged time, and thereby, the total duration of the flow test
239 can be prohibitively extended with additional injection ratios. The difficulty
240 in measuring phase saturations and consequent inaccuracy in measured
241 saturations can also be another disadvantage of using the steady-state
242 method (Honarpour et al., 1986).

243 In the unsteady-state method, a mobile phase present in a specimen is
244 displaced by another immiscible mobile phase generally injected at a
245 constant flow rate. The volume of the displaced phase and the differential
246 pressure across the specimen are concurrently monitored during the
247 injection of the displacing phase. The obtained data are then used to
248 calculate the relative permeability curve of each mobile phase over a

249 saturation range of either displacing or displaced mobile phase. The
250 “unsteady-state displacement test” can be completed quicker, which makes
251 it more practical than the steady-state method, as it does not need a
252 prolonged test time to attain equilibrated differential pressure and phase
253 saturation. On the negative side, however, to obtain relative permeability
254 curves, the unsteady-state method involves more intensive mathematical
255 calculations relying on applying Buckley-Leverett (Buckley and Leverett,
256 1942) immiscible displacement theory-based methods, such as JBN (Johnson
257 et al., 1959), JR (Jones and Roszelle, 1978), and Toth’s (Toth et al., 2002)
258 methods. These methods are developed based upon the assumptions that
259 the specimen tested would be negligibly affected by 1) core heterogeneity,
260 2) capillary force, and 3) capillary end effects, and the relative permeabilities
261 would then be calculated with monotonic fractional flow trends of displacing
262 and displaced fluid phases. When non-monotonic fractional flows develop,
263 which usually occur with severe heterogeneity in specimen, the calculated
264 relative permeability curve can be discontinuous (or irregular) (Sigmund and
265 McCaffery, 1979). Also, the methods, which neglect the capillary force in the
266 relative permeability calculation, cannot inherently account for capillary
267 heterogeneity and end effects that often appear in common cores during the
268 displacement test. To minimize the effect of neglecting capillary force in the
269 relative permeability calculation, the unsteady-state test should be
270 conducted with a high injection (or displacing) flow rate that creates a
271 differential pressure (across the specimen) large enough to overcome the

272 capillary force present in a specimen (Welge, 1952).

273

274 **3.2. Selection of Relative Permeability Test Method**

275 In general, neither of the two methods can provide both practicality
276 and accuracy of relative permeability measurement at the same time. With
277 the presence of hydrate in a specimen, the selection of an adequate relative
278 permeability test method becomes more challenging. This selection should
279 be made upon the comparative advantage of one method over the other
280 with respects to several factors we considered in the previous section.
281 However, for selection of the relative permeability test method in the
282 presence of hydrate, the feasibility in measuring reliable mobile phase
283 saturation is preferentially considered, since reliable mobile phase saturation
284 measurement defines the quality of a relative permeability relationship.
285 Measuring reliable phase saturation can be achieved in the unsteady-state
286 method far more easily as explained below.

287 In the steady-state test method, a delicate estimation process (e.g.,
288 weighing or CT-scanning methods) is needed to measure the mobile phase
289 saturations at the equilibrium condition. However, the presence of hydrate
290 in the core specimen makes the measurement more complicated. For
291 example, conventional weighing method generally requires removing cores
292 from the pressure chamber for the estimation of difference in core weights
293 whenever the equilibrium condition is reached at different injection ratios of
294 mobile phases (Richardson et al., 1952), but the removal obviously causes

295 disturbance of hydrate present in the core. X-ray CT-scanning (Schembre
296 and Kavscek, 2003; Vega and Kavscek, 2014) is often adopted to measure
297 the saturations of mobile phases at the equilibrium condition, but the
298 measurement would be challenging with the presence of hydrate due to the
299 difficulty in obtaining the end member base scans under gas- and liquid-
300 saturated conditions with identical locations of hydrate in pore space.
301 Hydrate pore habit can evolve as liquid saturation changes (Choi et al., 2014;
302 Lei et al., 2019), and as a result, the locations of hydrates can change.
303 Another difficulty in adopting X-ray CT-scanning for mobile phase saturation
304 measurements results from the similarity of gas hydrate and liquid (water) in
305 both density and X-ray transparency. So, it would be very difficult to
306 effectively separate hydrate and liquid (water) to estimate phase saturations
307 (Lei et al., 2018).

308 In the unsteady-state test method, the measurement of mobile phase
309 saturations can be attained with the production history of displaced mobile
310 phase. Phase separators are conventionally used to monitor the amount of
311 displaced phase over time. For HBS specimens, it can also be technically
312 possible to reliably estimate mobile phase saturations in a specimen by
313 monitoring the production history with a phase separator if overall hydrate
314 saturation can be kept constant during the displacement test. In this study,
315 therefore, the unsteady-state method is chosen over the steady-state
316 method as a relative permeability measurement method for HBS specimen
317 due to its relatively easy and quick estimation of phase saturations as well as

short overall test duration, even though it still shares the same challenges in coping with core heterogeneity, capillary force, and end effects that are present in hydrate-free sediments (HFS). Also, note that the short test duration of unsteady-state method can also be advantageous in reducing the possibility of hydrate saturation variation, which may increase under a prolonged coexistence of the three phases (hydrate, gas, and liquid) in a specimen.

4. Design of Experimental System

The experimental challenges and suggested mitigations to overcome these challenges are the main criteria to develop a practical experimental setup for the unsteady-state relative permeability test on HBS specimen. Figure 1 shows the experimental setup consisting of six major components: pressure chamber, differential pressure measurement system, pressure control system, temperature control system, flow control and measurement system, and immiscible fluid preparation system. The detailed descriptions and justifications for the choices of the experimental approach and systems developed are presented in the following subsections.

4.1. Pressure Chamber

A high-pressure aluminum chamber is incorporated into the system as a base testing cell for gas hydrate-bearing specimen preparation and conducting permeability tests. The pressure chamber (outer diameter of

12.1 cm × length of 43.8 cm) is equipped with a temperature controlling coolant jacket and capable of applying triaxial pressure conditions to the specimen: confining pressure through a stiff deformable rubber sleeve and axial pressure with a loading piston (Seol et al., 2014). The working pressure of the chamber is rated up to 21 MPa. The chamber uses a 5-mm thick rubber sleeve that is rigid enough to support a packed soil column and flexible enough to prevent injected fluid from flowing through the interface between its inner wall and the soil column (i.e., side-wall leakage) during the permeability test. Note that as shown in Figure 1, the pressure chamber is vertically set up during all the experimental procedures, especially to facilitate the liquid saturation of specimen and to minimize gas-liquid gravity segregation during the gas-liquid relative permeability test.

4.2. Differential Pressure Measurement System

A differential pressure transducer (DPT; 3051CD, Rosemount Inc.; accuracy of $\pm 0.04\%$ of span) is adopted to measure the differential pressure (ΔP) across the specimen during the permeability tests. The DPT is directly connected to the inlet and outlet faces of the specimen with tubing lines that are separate from the main flow lines (Figure 1). The separate ΔP tubing lines eliminate possible errors in the ΔP measurement, which occur when the ΔP tubing lines are connected to the main flow lines and the resistance of the portions of main flow lines that share the paths to/from the specimen with the ΔP tubing lines is large. In addition, a thin heating tip, made out of a

thermocouple with 0.25-mm diameter (TJC36-CASS-010U, Omega Inc.), is inserted into each end of ΔP tubing lines. The use of heating tips is to prevent the unintended hydrate formation in the ΔP tubing line ends by heating and thereby to ensure the measurement of ΔP , especially during the relative permeability test where the methane is injected into the brine-saturated specimen.

4.3. Pressure Control System

In order to independently control pore, radial, and axial pressures on the specimen, three syringe pumps (Pumps A, B, and C, respectively, in Figure 1; 500D, Teledyne ISCO) are connected to the corresponding pressure ports on the pressure chamber. Unlike radial and axial pressures, the pore pressure is designed to be controlled from both ends by injecting fluids on one end and simultaneously regulating the back pressure on the other end. A digitally-controlled dome-loaded back pressure regulator (BPR; DBPR-5HC, Coretest System Inc.) is installed at the end of downstream line to control the pore pressure. The BPR can control the pressure up to ~ 52 MPa with the allowable entry flow rate ranged from 0.01 to 15 ml/min. Note that absolute pressure transducers (Model 205, Setra Systems, Inc.; accuracy of $\pm 0.073\%$ of full scale) are used for the measurement of each pressure.

For the condition where both gas and liquid phases simultaneously flow out of the core specimen, a 1.5-liter liquid reservoir is installed before the BPR. The effluent flow is directed to the top port of the reservoir, and only

the liquid contained in the reservoir is released to the BPR through the bottom port of the reservoir. This reservoir helps improve the back-pressure control with reduced fluctuation by eliminating the chance of gas volume expansion and ice formation at the BPR. In this study, the reservoir is filled with a brine that has a salinity (8 wt % CaCl_2 solution) higher than that of the brine (5 wt % CaCl_2 solution) used to saturate the specimen and run single-phase (brine) permeability tests. With the brine having higher salinity, unintended hydrate formation can be avoided in the reservoir and BPR during the tests, since the test P-T condition is set near the hydrate stability boundary for 5 wt % CaCl_2 solution and the increase of salinity requires higher pressure/lower temperature for hydrate to form.

4.4. Temperature Control System

To prevent or minimize the change in gas hydrate saturation in the specimen during brine saturation process and permeability tests under a specific pressure, the temperatures of the specimen and surroundings need to be controlled. All the test equipment except for the gas cylinder is stationed inside an environmental chamber, within which the temperature is set at the actual specimen temperature (or test temperature). This helps avoid the hydrate formation and dissociation that can occur if the temperature of injected fluid is different from that of specimen.

The temperature of the specimen can be regulated further by a cooling bath that circulates coolant through an external jacket covering the main

body of the pressure chamber. The cooling bath is especially useful for adjusting specimen temperature below that of environmental chamber during hydrate formation and precisely controlling specimen temperature during the saturation process and permeability tests. As a note, to reduce the impact of ambient temperature fluctuation of the environmental chamber on specimen temperature, multiple layers of insulation material are placed around the cooling jacket of the pressure chamber. The specimen temperature is monitored by a K-type thermocouple (Omega Inc.) embedded 2.54-cm deep into the bottom of specimen. The standard deviation of specimen temperature readings calibrated in the range of 0 to 50 °C is about 0.05 °C.

The flow lines are covered with insulation material to help inhibit the lines from clogging by unintended hydrate formation that can occur if the lines are directly exposed to cooling air circulation. Inside the environmental chamber, it is always possible to have cooling air flow that comes directly from the air conditioning unit. If any signs of clogging appear by unintended hydrate formation, such as increasing line pressure, the suspected section of flow lines can be warmed with external heat sources to dissociate the hydrate. Note that the hydrate clogging causing line pressure increase usually happens on the downstream side where gas and liquid concurrently flow especially during the relative permeability test.

4.5. Flow Control and Measurement System

433 The pore fluid injection pump (Pump A in Figure 1 with 500-ml volume)
434 is used to supply gas (methane) into the specimen during the hydrate
435 formation and to inject liquid (brine) during the saturation of the hydrate-
436 formed specimen and the single-phase (brine) permeability test. The pore
437 fluid injection pump maintains **1)** pore pressure constant during the hydrate
438 formation with the outlet port of the pressure chamber closed or **2)** injection
439 flow rates constant during the single-phase permeability test together with
440 the back-pressure regulator (BPR) at the end of downstream line. The
441 volume capacity of the pump should be sufficient to complete hydrate
442 formation, brine injection, or a single-phase (brine) permeability test without
443 interruptions for refilling with the corresponding fluid. Note that during the
444 hydrate formation, brine saturation, and single-phase (brine) permeability
445 tests, the methane and brine flowing out of the pump are directed to enter
446 the vertically-standing specimen from the bottom.

447 During a gas-liquid drainage relative permeability test, injecting
448 displacing fluid (methane) needs to continue without interruptions until the
449 ΔP across the specimen and accumulated volume of displaced fluid (brine)
450 become stabilized. For the continuing injection of methane gas at a constant
451 flow rate, a high-pressure mini Coriolis mass flow controller (MFC; M12V10I,
452 Bronkhorst USA Inc.; accuracy of $\pm 0.5\%$ of reading for gas), directly
453 connected to a gas supply cylinder, is used to regulate the methane injection
454 into the brine-saturated specimen. The MFC directly regulates mass flow
455 rates and converts the regulated mass flow rates into volumetric flow rates

456 based on flowing fluid (methane) density that the MFC measures. It should
457 be noted that the accuracy of Coriolis MFC is generally known to be higher
458 than commonly used thermal MFC, so the reliability of measured ΔP and
459 accumulated volume of displaced fluid for the targeted flow rate can be
460 improved with the Coriolis type. The regulated methane flow then enters the
461 specimen from the top.

462 The volume measurement of displaced fluid flowing out of the
463 specimen needs to be made during the gas-liquid relative permeability test.
464 The measured fluid volumes are base inputs to estimate fluid saturations in
465 the specimen. A general phase separator can be used for the volume
466 measurement with visual volume reading or post-weighing the collected
467 fluid, but such subjective or indirect measurements can include errors. In
468 this study, a high-pressure sonic phase separator (SPS; two-phase; SFS-032,
469 Coretest System Inc.) is used between the pressure chamber and the liquid
470 (brine) reservoir on the downstream side for high accuracy volume
471 measurement (resolution of 0.06 ml) of displaced fluid (brine) under a
472 predetermined P-T condition. Sonic reflection from the interface between
473 two immiscible effluent fluids (methane + brine) allows continuous volume
474 measurements of displaced fluid. The accurate measurement of volume of
475 displaced fluid reduces the error in estimating mobile phase saturations that
476 govern the relative permeabilities of the mobile phases.

477 The volume of effluent fluids (methane + brine) flowing from the
478 specimen can be estimated using a high-pressure Coriolis mass flow meter

479 (MFM; M12, Bronkhorst USA Inc.; accuracy of $\pm 0.2\%$ and $\pm 0.5\%$ of reading
480 for liquid and gas, respectively), which is connected either to the upper
481 outlet port of the SPS for drainage relative permeability test or to the lower
482 outlet port for imbibition test. For this study, we use the drainage test
483 configuration. With the drainage test configuration, only methane gas that
484 occupies the upper part of the SPS can exit the SPS through the upper outlet
485 port as soon as the effluent fluids flowing from the specimen enters the SPS
486 through the upper inlet port. The volume of methane exiting the SPS should
487 be equivalent to that of effluent fluids entering the SPS, because the
488 pressure of the SPS is maintained constant by a constant back pressure.
489 Therefore, the mass flow rate and density of the exiting methane, measured
490 by the MFM, can be used to calculate the volume of effluent fluids (“methane
491 + brine”) over time. With the volume of effluent fluids (“methane + brine”)
492 estimated by the MFM and the volume of displaced fluid (“brine” in drainage
493 test) measured by the SPS, the volume of displacing fluid (“methane” in
494 drainage test) entering the SPS can be calculated as well. Also, unintended
495 hydrate formation and dissociation in the specimen and flow lines that
496 possibly occur during the tests can be noticed by monitoring the change in
497 the mass flow rate with the MFM.

498

499 **4.6. Immiscible Fluid Preparation System**

500 It is important to keep the hydrate saturation of a HBS specimen
501 steady during the entire course of experiment, including the step of

502 saturating specimen with liquid (brine), single-phase (brine) permeability
503 test, and gas-liquid (methane-brine) relative permeability test. To avoid
504 hydrate saturation changes, the methane and brine need to be pre-saturated
505 with each other under the test P-T condition before their injection into the
506 specimen, which also allows for immiscible displacement condition during
507 the relative permeability test. Another pump (Pump D; 500D, Teledyne
508 ISCO), named the fluid mixing pump, is implemented into the test setup to
509 saturate the brine with methane before the brine is injected into the
510 specimen for the brine saturation of specimen and the single-phase
511 permeability test. The fluid mixing pump (Pump D) is first filled with the
512 brine and connected to the pore fluid injection pump (Pump A) that contains
513 methane. Then, the connected two pumps exchange the two fluids back and
514 forth to equilibrate the two fluids with each other. After three times of fluid
515 exchanges, the residual methane is removed to the fluid mixing pump, and
516 only the methane-saturated brine is left in the pore fluid injection pump for
517 its injection into the specimen. To moisten methane with water vapor for the
518 gas-liquid relative permeability test, a 50-ml reservoir half-filled with brine is
519 installed on the outlet side of the MFC. The methane flow regulated by the
520 MFC is directed to flow into the bottom of the reservoir, pass through the
521 brine, and then exit through the top, so that the methane becomes damp
522 before entering the specimen.

523

524 **5. Test Procedure**

525 A test procedure has been developed to sequentially conduct single-
526 phase (brine) permeability and gas-liquid (methane-brine) drainage relative
527 permeability tests on a single specimen with and without gas hydrate using
528 the developed experimental system. The following sections introduce the
529 details of the test procedure that include a specimen preparation method as
530 well as the sequence of permeability tests.

531

532 **5.1. Hydrate-Bearing Specimen Preparation**

533 A HBS specimen is prepared to have a hydrate pore habit that is
534 typically found in natural HBS, i.e., pore-filling, load-bearing or patchy type,
535 rather than cementing type (Konno et al., 2015a; Santamarina et al., 2015).
536 In the following subsections, the procedure of specimen preparation is
537 described step by step from the host sediment formation to the brine
538 saturation of the HBS specimen.

539

540 **5.1.1. Host Sediment Preparation**

541 As a main substrate for the HBS specimen, dry silica sand (F110;
542 median particle size, $D_{50} = 120 \mu\text{m}$) is mixed with kaolinite clay (5% by
543 weight; $D_{50} = 1 \mu\text{m}$). Kaolinite clay is added to mimic natural sandy
544 sediments, which generally contain fine particles (Boswell et al., 2009; Ito et
545 al., 2015). Deionized water is added to form a partially-saturated sediment
546 mixture with a water content of 9.3 wt %. The amount of water added in the

547 mixture determines the initial hydrate saturation of the specimen, i.e., 40-
548 45% in the sediment mixture with 0.34-0.37 porosity. A paper filter (Grade
549 P5; particle retention = 5 to 10 μm ; Herzberg flow rate = 60 ml/min, which is
550 equivalent to the permeability of 39.4 mD) is placed on top of the bottom
551 end cap of the testing cell to prevent the loss of soil particles and hydrates
552 during the subsequent soil packing, specimen saturation, and permeability
553 tests. As a note, more caution should, however, be taken to apply such
554 filters directly on the specimen especially when a highly permeable
555 specimen is tested and the fine content in the specimen is high, because the
556 permeability of the filter can cause a significant underestimation in the
557 permeability measurement of specimen and the filters can be clogged by
558 fines during fluid flow. The partially-saturated sediment mixture is then
559 packed into a round rubber sleeve (I.D. = 50.8 mm) sitting on the bottom
560 end cap of the testing cell. The dimensions and index properties of the
561 specimen obtained after packing are shown in Table 1.

562

563 **5.1.2. Hydrate Formation**

564 Methane hydrate is formed in the specimen by employing the brine-
565 injection and warming-cooling method (Choi et al., 2014). The hydrate
566 formation method consists of three main steps: **1)** initial hydrate formation
567 in the partially water (not brine) saturated specimen by raising the pore
568 pressure (u) to 6.89 MPa with methane injection (i.e., under excess-gas
569 condition), lowering the specimen temperature to $\sim 4^\circ\text{C}$, at which the P-T of

specimen is positioned well within the hydrate stability boundary for water, and subsequently providing the specimen with methane keeping the pore pressure constant; **2**) slow injection of methane-charged brine (5 wt % CaCl_2 solution; ~ 5 pore volumes) into the HBS specimen under a controlled P-T condition of 6.89 MPa and $\sim 8^\circ\text{C}$, which is still within the hydrate stability boundary for water; and **3**) a temperature warming-cooling cycle ($\sim 12^\circ\text{C}$ to $\sim 2^\circ\text{C}$) on the brine-filled HBS specimen in a closed system. With this method, hydrate forms in the specimen filling in brine-saturated pore spaces, mostly being off sediment particle contacts, which was proven with wave velocity measurements in our previous study (Choi et al., 2014). Once the warming-cooling step is completed as shown in Figure 2, the pore pressure is adjusted to 6.89 MPa with methane-saturated brine injection or pore brine release (depending on the pore pressure attained after the warming-cooling step), while the temperature to $\sim 8^\circ\text{C}$. The P-T condition of 6.89 MPa and $\sim 8^\circ\text{C}$ is selected to position the system condition slightly outside the hydrate stability boundary for 5 wt % CaCl_2 solution (6.89 MPa and 7.7°C). The selection of the P-T condition is intended to prevent or minimize the change in overall hydrate saturation of the specimen during the brine injection and the subsequent permeability tests (Choi et al., 2014). During hydrate formation, the temperature of environmental chamber is set at $\sim 8^\circ\text{C}$, and the effective confining stress (σ'_o) is maintained at ≤ 0.69 MPa. After the completion of hydrate formation and P-T adjustment, additional methane-charged brine (~ 5 pore volumes) is injected into the HBS specimen to ensure

its full saturation with the brine. Table 1 shows the P-T condition and hydrate saturation (S_h) of the specimen before the permeability tests. Note that the hydrate saturation in the specimen is estimated with the amount of gas collected during the later hydrate dissociation conducted after the completion of permeability tests.

5.2. Permeability Tests

The sequence of steps applied in the permeability tests includes: **1)** an effective permeability test with brine on the HBS specimen; **2)** an unsteady-state drainage relative permeability test on the HBS specimen; **3)** dissociation of hydrate and re-saturation of the HFS specimen with brine (~5 pore volumes); **4)** an intrinsic permeability test with brine on the HFS specimen; and **5)** an unsteady-state drainage relative permeability test on the HFS specimen. For all the permeability tests, the P-T condition of specimen is set at 6.89 MPa and ~8 °C.

5.2.1. Single-Phase Permeability Test

Steady-state single-phase permeability tests (i.e., effective and intrinsic permeability tests on HBS and HFS specimens, respectively) are conducted by injecting methane-charged brine into the brine-saturated specimen. The brine is injected into the specimen at multiple volumetric flow rates (q ; 0.5 to 8 ml/min) by the pore fluid injection pump (Pump A). The ΔP across the specimen is measured at each flow rate, when a stable ΔP

level is attained (Figure 3).

5.2.2. Gas-Liquid Relative Permeability Test

Gas-liquid relative permeability tests on the HBS and HFS specimens are conducted based on the unsteady-state drainage method. Moistened methane is injected into the brine-saturated specimen at a flow rate of 8 ml/min regulated by the MFC. The methane injection flow rate mimics the gas flow rate (normalized to flow through an interface area unit [m^2]) predicted to occur near the wellbore of a producing gas hydrate reservoir, such as the Site NGHP-02-16 in Area-B of the Krishna-Godavari Basin in offshore India (Myshakin et al., 2019). Key experimental data to collect during the relative permeability tests include the ΔP and the volume of brine displaced by the injected methane, which are monitored until their variations become stabilized.

6. Results

Fundamental experimental data, such as pressure, temperature, and mass flow rate, monitored during single-phase permeability and gas-liquid relative permeability tests are provided to present the reliability of the proposed experimental system and procedures. On the other hand, key experimental data, such as ΔP and volume of displaced brine, are interpreted to obtain the permeabilities, and the results are compared to reveal the effects of hydrate on the permeabilities and analyzed to understand their

physical implications to the fluid flow in the HBS.

6.1. Single-Phase (Brine) Permeability Test

The single-phase permeability of the specimen, either effective or intrinsic permeability depending on the presence of hydrate, is further used as a base to estimate relative permeability of mobile fluids. Figure 3 shows the ΔP across the specimens measured at various injection flow rates (q) during the single-phase (brine) permeability tests. It is shown in Figure 3 that ΔP increases linearly with increasing q for both HBS and HFS specimens. The linearity with R^2 -values of > 0.990 reflects the pore structure stably conserved during the brine injection, meaning that under the adopted P-T condition, noticeable changes in hydrate saturation and hydrate pore habit are prevented or minimized in the specimen. Also, the linearity suggests that the clogging of the specimen and paper filter by fines (clay particles) migration or hydrate formation is likely avoided during the tests. Note that the flocculation of clay particles in the CaCl_2 brine possibly helps limit the clay migration under the applied injection flow rates.

The ΔP and q data for each specimen are then used to calculate their single-phase permeabilities (k) using Darcy's law as follows:

$$k = \frac{q\mu L}{A\Delta P} (1)$$

where μ = dynamic viscosity of fluid; L = length of specimen; and A = cross-section area of specimen. Effective and intrinsic permeabilities are calculated at different flow rates and averaged as shown in Table 2. As

662 expected, the presence of hydrates ($S_h = 42.0\%$) in the specimen reduces
663 the permeability of specimen. The permeability reduction index (N) of 3.09,
664 calculated from $k_e/k_0 = (1 - S_h)^N$ (where k_e and k_0 = effective and intrinsic
665 permeabilities, respectively), indicates that patchy type hydrates with a
666 weak cementation with surrounding soil particles may exist in the specimen
667 (Dai and Seol, 2014). As a note, applying paper filters (with the permeability
668 of 39.4 mD) on both ends of specimen leads to negligible errors in the
669 estimation of permeability in this study. Accounting for the paper filters
670 results in actual permeabilities of the HBS and HFS specimen being about
671 0.9% and 5.0% higher than those shown in Table 2, respectively.

672

673 **6.2. Gas-Liquid Relative Permeability Test**

674 **6.2.1. P-T Monitoring**

675 During the relative permeability test, unintended hydrate formation or
676 dissociation can occur in the specimen when the P-T condition of the
677 specimen drifts into or out of the hydrate stability zone. Figure 4 shows the
678 outlet pore pressure and temperature of HBS specimen monitored during the
679 relative permeability test. As shown, the monitored P-T values fluctuate, and
680 their average values (6.94 MPa and 8.2 °C) deviate from the targeted P-T
681 (6.89 MPa and ~8 °C). However, the overall trend of monitored P-T moves
682 within the standard deviation of 7 kPa and 0.1 °C, and their deviation from
683 the targeted P-T is less than +0.05 MPa and +0.2 °C, which reveal that the
684 outlet pore pressure and temperature of specimen are stably controlled.

Note that there are two noticeable features observed in pore pressure and temperature data. Several small spikes on outlet pore pressure indicate short-lived flow pathway blockages, which seem to be caused by unintended hydrate formations in the downstream flow line when the temperature cycle of environmental chamber reaches its cooling trough. Moderate cyclic changes in specimen temperature are caused by fluctuations of ambient temperature in the environmental chamber.

6.2.2. Mass Flow Rate Monitoring

Figure 5 shows the mass flow rate of methane (in green) vented from the sonic phase separator (SPS) during the relative permeability test with the HBS specimen. While there are several small spikes in the mass flow rate resulting from temporary clogging episodes with unintended limited hydrate formation, its overall trend (average mass flow rate = 0.55 g/min; standard deviation = 0.03 g/min) is consistent with the methane injection rate (in red) into the specimen throughout the test. The consistency indicates that hydrate saturation is well maintained.

6.2.3. Differential Pressure and Volume of Displaced Brine

Figure 6 shows the variation in ΔP and the accumulated volume of brine displaced from the brine-saturated specimen (V_k) by methane injection. The early increase in ΔP occurs because of the entry of the residual brine from injection tubing line into the brine-saturated specimen. Note that the

708 injection tubing line is fully filled with brine after the previous single-phase
709 (brine) permeability test. Once the methane reaches the inlet face of the
710 specimen and the capillary entry pressure is overcome, methane starts to
711 flow into the specimen. As soon as methane starts flowing in and displacing
712 the brine from the specimen, ΔP drops rapidly. The curves of the drop of ΔP
713 and the increase in accumulated volume of displaced brine (V_k) gradually
714 flatten as the methane injection progresses. The data curves of HBS and
715 HFS specimens become nearly flat after about 8 and 4.5 pore volumes of
716 methane injection, respectively.

717 The HFS specimen, mostly composed of F110 sand with the median
718 particle size (D_{50}) of 120 μm , has the averaged pore throat size of about 12
719 μm , i.e., about one tenth of diameter of sediment particle (Hunt et al., 1988),
720 and its capillary entry pressure can be estimated about 23 kPa ($P_{c,e} \approx 2\sigma/r_t$,
721 where σ = interfacial tension between methane and brine, ~ 70 mN/m and r_t
722 = radius of pore throat, ~ 6 μm), which is equivalent to the ΔP at the onset of
723 methane entry into the specimen as shown in Figure 6b. This indicates the
724 paper filter used on the specimen may not have much influence on the early
725 ΔP development for the HFS specimen, which is also backed up by the
726 particle retention size (or pore size) of the paper filter (5 to 10 μm) that is
727 close to the pore throat size of the specimen (~ 12 μm). Also note that the
728 paper filter may have no influence on the early ΔP development for the HBS
729 specimen (Figure 6a), since the averaged pore throat size of the specimen
730 with the presence of hydrate is smaller than the particle retention size of the

731 paper filter.

732 To accurately estimate the saturation of each fluid phase in the
733 specimen, the arrival time of injected methane at the inlet face of specimen
734 must be known. The arrival time of the methane can be estimated by
735 counting the time that the V_k (measured by the SPS from the start of
736 methane injection) takes to become equivalent to the known internal volume
737 of the injection tubing line up to the inlet face of the specimen (note: the
738 injection tubing line is fully filled with brine at the start of methane injection).
739 The estimated arrival times of injected methane are ~26 and ~19 seconds
740 for the tests on the HBS and HFS specimens, respectively, as shown in Figure
741 6. The discrepancy in the arrival time (between ~26 and ~19 seconds) can
742 occur when the time interval to reach the targeted injection flow rate (8 ml/
743 min) is different. The time interval varies depending on the flow-controlling
744 parameters set in the MFC.

745 The time for the injected methane to break through the specimen can
746 easily be recognized with the V_k plot where the early linear increase of V_k
747 turns into the nonlinear increase (as indicated in Figure 6, at 78 and 132
748 seconds on the V_k data of HBS and HFS specimens, respectively).
749 Recognizing the break-through point is important, since the calculations of
750 unsteady-state relative permeability based on Buckley-Leverett theory are
751 made with the analysis of fractional flow data that are only obtained after
752 the break-through.

753 Note that while the ΔP data are measured with the DPT located right on

754 the specimen, the V_k data are measured with the SPS located on the
755 downstream side away from the specimen. The V_k reflects the saturations of
756 mobile fluids in the specimen that influence the ΔP . However, the V_k is
757 measured with a time delay relative to the corresponding ΔP , due to the
758 difference in data measurement location. The two data sets of ΔP and V_k ,
759 therefore, need a temporal matching to each other (synchronization). The
760 time delay can be estimated by measuring the travel time of effluent fluid
761 from the outlet face of specimen to the SPS. The measurement of the travel
762 time can be experimentally attainable by counting the time elapsed for “the
763 accumulated volume of effluent fluid (brine) that has flowed out of the
764 specimen since the arrival of the methane at the inlet face of the specimen”
765 to become equivalent to “the known internal volume of tubing line from the
766 outlet face of the specimen to the inlet port of the SPS”. In the current test
767 setup, the accumulated volume of effluent fluid can be measured by the
768 MFM. The measured travel time (i.e., time delay) is about 42 and 43 seconds
769 for the tests on HBS and HFS specimens, respectively. Consequently, in case
770 of the test on the HBS specimen (Figure 6a), the V_k at 68 seconds (= 26
771 seconds + 42 seconds) becomes the initial data point for the temporal
772 matching with the ΔP at 26 seconds that corresponds to the arrival of
773 methane front at the inlet face of the specimen. The ΔP and V_k data
774 collected at and after the temporal matching points are used for the
775 subsequent relative permeability calculation.

776

6.2.4. Relative Permeability Curves

Toth's method, a direct interpretation method (Toth et al., 1998; Toth et al., 2002) developed based on Buckley-Leverett theory, is adopted for the relative permeability calculation. Toth's method employs four statistical parameters (a , b , a_1 , and b_1) obtained from two linear regression equations, which are created using the data of accumulated volume of displaced fluid (V_k ; brine) and differential pressure (ΔP) across the specimen obtained at and after the break-through of the fluid (methane) injected into the specimen:

$$\frac{V_i(t)}{V_k(t)} = a + b \left(\frac{V_i(t)}{V_p} \right) (t \geq t_a) \quad (2)$$

$$\Delta P(t) = a_1 \left(\frac{V_i(t)}{V_k(t)} \right)^{b_1} (t \geq t_a) \quad (\text{linearly fitted in log-log scale}) \quad (3)$$

where V_i = accumulated volume of injected fluid (methane); V_p = pore volume; t = time elapsed from the onset of the invasion of injected fluid (methane) into the specimen; and t_a = break-through time. With the linear data regression, Toth's method is considered more simple and applicable, compared to the conventional methods that involve non-linear regressions and graphical techniques (Johnson et al., 1959; Jones and Roszelle, 1978), particularly when data fluctuation is evident as shown in Figure 6. The data regressions to obtain the Toth's statistical parameters are shown in Figure 7, and the obtained parameters are listed in Table 2 along with other parameters necessary to calculate relative permeability curves, such as

798 specimen dimension, effective porosity, flow rate of fluid (methane) injection,
 799 initial saturation of displacing fluid (methane), dynamic viscosities of fluids
 800 (methane and brine), and absolute permeabilities (effective and intrinsic
 801 permeability for HBS and HFS specimens, respectively). Relative
 802 permeability curves are then calculated, as shown in Figure 8, by plugging
 803 the parameters into relevant Toth's equations (Toth et al., 2002).

$$804 \quad S_{d,2} = b \left[\frac{\frac{V_i(t)}{V_p}}{a + b \frac{V_i(t)}{V_p}} \right]^2 + S_{d,i} \quad (4)$$

$$805 \quad M_{d,2} = \frac{\left[a + b \frac{V_i(t)}{V_p} \right]^2}{a} - 1 \quad (5)$$

$$806 \quad f_{d,2} = \frac{M_{d,2}}{M_{d,2} + 1} \quad (6)$$

$$807 \quad f_{k,2} = \frac{1}{M_{d,2} + 1} \quad (7)$$

$$808 \quad Y(S_{d,2}) = \frac{qL}{kA a_1 + (1 - b_1) \left(\frac{V_i(t)}{V_p} \right)^{b_1}} \quad (8)$$

$$809 \quad k_{r,d} = \mu_d f_{d,2} Y(S_{d,2}) \quad (9)$$

$$810 \quad k_{r,k} = \mu_k f_{k,2} Y(S_{d,2}) \quad (10)$$

811 where $S_{d,2}$ = saturation of displacing fluid (methane) at outlet face of
 812 specimen; $S_{d,i}$ = initial saturation of displacing fluid (methane); $M_{d,2}$ =
 813 mobility ratio of displacing fluid (methane) at outlet face of specimen; $f_{d,2}$ and

814 $f_{k,2}$ = fractional fluid flows of displacing (methane) and displaced (brine)
815 fluids, respectively; k = absolute permeability (i.e., effective and intrinsic
816 permeabilities for HBS and HFS specimens, respectively); $Y(S_{d,2})$ = total
817 mobility function; $k_{r,d}$ and $k_{r,k}$ = relative permeabilities of displacing
818 (methane) and displaced (brine) fluids, respectively; and μ_d and μ_k = dynamic
819 viscosities of displacing (methane) and displaced (brine) fluids, respectively.

820 As shown in Figure 8 (solid lines), the residual brine saturations
821 obtained with about 8 and 4.5 pore volumes (V_i/V_p) of methane injection are
822 0.933 and 0.696 for the HBS ($S_h = 42.0\%$) and HFS specimen, respectively.
823 The residual brine saturation of HBS specimen is higher than that of HFS
824 specimen, even though more of methane (8 pore volumes) is injected into
825 the HBS specimen. The steeper drop and rise of brine and methane relative
826 permeability, respectively, are also observed for the HBS specimen with the
827 earlier attainment of the residual state of brine in the specimen.

828 Meanwhile, using the same Toth's fitting parameters, relative
829 permeability values are extrapolated (dotted lines in Figure 8) as if 100 pore
830 volumes of methane is injected. As a result, the residual brine saturations
831 are reduced to 0.932 and 0.656 for HBS ($S_h = 42.0\%$) and HFS specimen,
832 respectively. The reduction in the residual brine saturation after the virtually
833 extended methane injection appears to be negligible, suggesting that the
834 actual volumes of methane injection (~ 8 and ~ 4.5 pore volumes for HBS and
835 HFS specimen, respectively) would be reasonable to bring the brine residing
836 in the specimen to its residual state.

837

838 **7. Discussion**

839 Maintaining the hydrate saturation of the HBS specimen during the
840 relative permeability test is the most challenging task in this study. We
841 discuss how it is accomplished with the controlled P-T condition. In addition,
842 we discuss the possible cause and remedy of the high residual brine
843 saturation observed in the relative permeability curve of the HBS specimen.

844

845 **7.1. Preservation of Hydrate Saturation with Controlled P-T** 846 **Condition**

847 In Figure 2, the P-T condition at the outlet face of the HBS specimen
848 during the relative permeability test is plotted in comparison with that
849 observed during the warming-cooling step of hydrate formation in the
850 specimen within the closed system. As shown in the inset in Figure 2, during
851 the warming step, a noticeable pressure increase, i.e., an indication of
852 hydrate dissociation, appears to be delayed maintaining ~ 6.89 MPa until the
853 temperature reaches ~ 8.4 °C, although the P-T is already outside the
854 hydrate stability boundary (~ 7.7 °C at 6.89 MPa). This delay may occur
855 because of the combined effects of: **1)** brine salinity reduction associated
856 with fresh water release by minor or localized hydrate dissociations, **2)** minor
857 pressure increase related to gas release, and **3)** temperature decrease owing
858 to the endothermic nature of the hydrate dissociation reaction (Choi et al.,
859 2014). Minor or localized hydrate dissociation-reformation processes occur

860 quickly leading to the delay in dissociation, since there is no induction time
861 associated with hydrate lattice formation when water bearing the “memory
862 effect” is promptly available from a previous occurrence of dissociation
863 (Myshakin et al., 2009). Once the driving force of hydrate decomposition
864 created by the temperature increase becomes large enough to break such
865 thermodynamic metastable condition, the continuous hydrate dissociation
866 occurs.

867 The P-T conditions of the HBS specimen throughout the relative
868 permeability test (Figure 2 inset; purple and red plots for inlet and outlet
869 sides of the specimen, respectively) are outside the hydrate stability zone,
870 but they do not reach the thresholding P-T condition (~ 8.4 °C at 6.89 MPa)
871 that initiates the continuous hydrate dissociation during the warming step.
872 The metastable condition also likely occurs and limits hydrate dissociation,
873 preventing noticeable changes in hydrate saturation at both inlet and outlet
874 face of the specimen during the relative permeability test. All of this
875 indicates that under the P-T condition of 6.89-7.10 MPa and 7.8-8.4 °C, the
876 gas-liquid multiphase flow test is executed without significant unintended
877 hydrate formation and dissociation in the HBS specimen, especially when the
878 5 wt % CaCl_2 brine is used as a liquid phase to saturate the specimen. The
879 liquid phase salinity buffers hydrate stability by creating a thermodynamic
880 metastable condition, allowing the relative permeability measurements.

881 As an additional piece of evidence of the preservation of hydrate
882 saturation with controlled P-T condition, it should also be noted that the

methane amount consumed during the initial hydrate formation (~0.338 mol) appears to closely match that collected during the hydrate dissociation conducted after the relative permeability test (~0.326 mol). The hydrate saturations calculated based on the measured methane amounts are about 43.6% and 42.0% for the cases after initial hydrate formation and after relative permeability test, respectively. When all possible sources of experimental error are taken into consideration, the difference seems to be negligible. Therefore, it can possibly claimed that the hydrate saturation of the specimen has been preserved throughout the brine saturation, single-phase (brine) permeability test, and relative permeability test under the controlled P-T condition.

7.2. Residual Brine Saturation of HBS Specimen

The relative permeability curves (Figure 8) show that the residual brine saturation of the HBS specimen is higher than that of the HFS specimen. The presence of hydrate in the specimen reduces pore size while increasing total surface area of solid matrix (sediment and hydrate). Both of these factors increase the capillary retention of brine. As seen in imaging studies (Rees et al., 2011; Seol and Kneafsey, 2011), the hydrate increases sediment heterogeneity, solid matrix size distribution, and pore size distribution, which can also lower displacement efficiency. Meanwhile, the low viscosity ratio of injected methane to brine ($M = 8.452 \times 10^{-3} < 1$) inherently results in viscous instability that would incur preferential pathways (i.e., fingering) in

906 the saturated sediment. The advance of displacing fluid (methane) in a
907 fingering pattern leads to an early break-through and in turn, lowers break-
908 through production of displaced fluid (brine), contributing to the low
909 displacement efficiency. Once gas pathways are developed, it is difficult to
910 improve such low displacement efficiency any further.

911 Relative permeability is also dependent on injection flow rates when
912 the viscous instability and capillary heterogeneity of a porous medium are
913 significant (Huppler, 1970; Peters and Khataniar, 1987). A capillary number
914 of $\sim 3.316 \times 10^{-8}$ ($N_c = \mu v / \sigma$, where μ = dynamic viscosity of displacing
915 phase, i.e., methane, 1.234×10^{-5} Pa·sec; v = interstitial flow velocity, 1.881
916 $\times 10^{-4}$ m/sec; and σ = interfacial tension between methane and brine, ~ 70
917 mN/m) is calculated under the current experimental condition shown in
918 Tables 1 and 2. Such a low N_c ($< 10^{-5}$) suggests that capillary forces are
919 dominant for the fluid flow in the specimen as compared to viscous forces.
920 The low capillary number ($N_c = \sim 3.316 \times 10^{-8}$) combined with the
921 unfavorable viscosity ratio ($M = 8.452 \times 10^{-3} < 1$) reveal that capillary
922 fingering likely occurs during the relative permeability test (Lenormand,
923 1990; Lenormand et al., 1988; Sinha and Wang, 2007). Also note that the
924 unfavorable viscosity ratio may cause the relative permeability of displaced
925 fluid (brine) to be underestimated from its true value which is generally
926 considered to be obtained with the steady-state method (Maini et al., 1990).

927 In typical sandy HBS constituting high quality reservoirs, the
928 irreducible water saturations typically exist within a range of 0.05-0.30 based

on interpretations of NMR-log data (Myshakin et al., 2011). Those numbers represent capillary-bound, clay-bound, and structural water that is considered immobile over a time period of gas production from a hydrate reservoir. The high numbers of residual (or pseudo irreducible) brine saturation found in this pore-scale laboratory test preclude direct application of the deduced relative permeability data in reservoir simulations. Increasing the viscous force by applying a higher methane injection flow rate may reduce the high residual brine saturation values shown in Figure 8. The higher injection flow rate will increase the ΔP across the specimen and may also reduce the effect of capillary heterogeneity on the high residual brine saturation by allowing the injected methane to invade smaller pore spaces. However, the application of a higher injection flow rate should be carried out in consideration of higher potential of particle migration in the specimen, turbulent flow, and extra hydrate formation especially at the inlet face of the specimen, as well as the capacity of instruments for larger flow rate and volume.

8. Summary and Conclusion

This work is one of the first experimental studies of two-phase (methane-brine) flow in brine-saturated HBS samples prepared to mimic natural settings and proposes a novel experimental system and procedure to obtain relative permeability of gas (methane) and liquid (brine) in HBS. This study discusses **1)** technical challenges in conducting the gas-liquid relative

952 permeability test on HBS, **2)** experimental methodology and setup to
953 overcome the technical challenges, **3)** preparation of a sandy HBS specimen
954 with a natural-like pore habit and execution of single-phase (brine)
955 permeability and gas-liquid (methane-brine) relative permeability tests,
956 particularly the latter with the unsteady-state drainage displacement
957 method, and **4)** estimation of the relative permeability curves and residual
958 saturation calculated by Buckley-Leverett (B-L)-theory-based Toth's method
959 (Toth et al., 1998; Toth et al., 2002).

960 The most difficult experimental challenge for a successful gas-liquid
961 relative permeability test on HBS is to maintain the initial hydrate saturation
962 and configuration under the dynamic flow condition. Key approaches used to
963 maintain the hydrate saturation in this study include:

- 964 • Using brine (5 wt % CaCl_2) to saturate the specimen,
- 965 • Applying the test P-T condition (6.89-7.10 MPa and 7.8-8.4 °C) set
966 slightly outside the hydrate stability boundary (6.89 MPa and 7.7 °C) at
967 the salinity level used in brine,
- 968 • Pre-equilibrating methane and brine with each other under the test P-T
969 condition before their injection into the specimen.

970

971 Other experimental solutions to conduct reliable gas-liquid relative
972 permeability tests on HBS are also proposed in this study as follows:

973

974 Instrumental solutions for better maintenance of the applied P-T condition

975 are:

- 976 • A large liquid reservoir (1.5-liter) installed before the back pressure
977 regulator to reduce the pore pressure fluctuations,
- 978 • A cold room to accommodate the entire test setup under the
979 controlled temperature condition,
- 980 • Additional cooling jacket on the pressure chamber for temperature
981 control of the specimen.

982

983 Approaches to avoid hydrate clogging in flow lines are:

- 984 • Covering tubing lines with insulation materials to avoid direct exposure
985 to ambient cooling air of the environmental chamber,
- 986 • Using spot heating sources, such as heating tip, gun, or even warming
987 by hand, to heat up the hydrate-clogging-prone sections, such as ΔP
988 pressure line loop and downstream flow line,
- 989 • Using high salinity brine (8 wt % CaCl_2) to fill up the 1.5-liter reservoir
990 to avoid hydrate clogging in the downstream line up to the back-
991 pressure regulator.

992

993 Solutions for other challenges are:

- 994 • Using high-pressure sonic phase separator to measure the volume of
995 displaced fluid under the test P-T condition for accuracy,
- 996 • Saturating the specimen with CaCl_2 brine to limit clay migration by
997 forming larger clay flocs and using a paper filter (Grade P5; particle

998 retention = 5 to 10 μm) to prevent any particle loss from the
999 specimen,

- 1000 • Selecting a high gas injection flow rate from the near-wellbore area of
1001 a simulated producing reservoir to reduce the adverse capillary effects
1002 on the relative permeability test results.

1003

1004 While overcoming many technical difficulties associated with
1005 conducting the unsteady-state relative permeability test in HBS, this study
1006 reveals the low displacement efficiency in HBS resulting in high residual
1007 brine saturations. Besides the viscous instability which is inherent for any
1008 gas-liquid drainage displacement tests, one possible reason for the low
1009 displacement efficiency in HBS compared to HFS can be the shift of a pore
1010 size distribution toward a wide range due to the appearance of small pores in
1011 the presence of hydrate. Consequently, a strong capillary heterogeneity can
1012 develop in HBS likely contributing to the high residual saturation. The
1013 verification of this issue is outside the scope of this study, but it is worthy of
1014 investigation in future. The results obtained in this work and summarized
1015 above, nevertheless, pave a way to further improvements of experimental
1016 apparatus and test execution framework, and bring the understanding of the
1017 complex two-phase flow phenomenon in HBS.

1018 Further improvements on the test setup and method in future may
1019 include **1)** improvement on controlling gas injection flow rate for the
1020 drainage displacement test: it is hard to smoothly increase the gas injection

1021 flow rate to a targeted level without an overshoot with the current MFC, **2)**
1022 increase in size of brine reservoir that is used to reduce the fluctuation of
1023 back pressure: the total amount of gas injection can be limited within 1.5
1024 liter with the current reservoir; and **3)** improvement on temperature control
1025 in the environmental chamber: a temperature fluctuation of the chamber
1026 causes the fluctuation of the specimen temperature and may lead to the
1027 unintended hydrate formation in flow lines.

1028 Upon the experimental results observed in this study, the future
1029 investigation may involve **1)** inverse modeling simulations to calculate curve
1030 fitting parameters of conventional or newly developed relative permeability
1031 models using obtained test results, **2)** further relative permeability tests with
1032 higher flow rates of methane injection to mitigate the effect of capillary
1033 heterogeneity on the results, and **3)** experimental measurements of
1034 wettability of hydrates with respect to brine under equilibrium conditions of
1035 brine-hydrate-methane.

1036

1037 **Credit Author Statement**

1038 Jeong-Hoon Choi, Conceptualization, Methodology, Formal analysis,
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1055

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1290 **Table 1.** Core physical properties and experimental conditions.
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Host sediment	silica sands (F110, mean particle size = 120µm) + 5 wt % kaolinite clays (mean particle size = 1µm)
Initial gravimetric water content, W (%)	9.3
Diameter × Length, $D \times L$ (mm)	50.8 × 153.7
Initial nominal pore volume, $V_{p,0}$ (ml)	109.6
Initial porosity, n_0	0.35
Hydrate saturation, S_h (%)	42.0
Pore pressure, u (MPa)	6.89
Temperature, T (°C)	~8
Effective confining stress, σ'_o (MPa)	0.69

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Table 2. Experimental parameters for permeability calculations.

Specimen	Hydrate-bearing ($S_h = 42.0\%$)	Hydrate-free
Dynamic viscosity of brine, μ_{brine} (Pa·sec)	1.460E-03 ^(a)	
Dynamic viscosity of methane, $\mu_{methane}$ (Pa·sec)	1.234E-05 ^(b)	
Injection flow rates for single-phase perm. test, q_{brine} (ml/min)	0.5→1→0.5→2→1→4 →2→8→4→2→1→0.5	2→4→2→8→4→2
Effective permeability, k_e (mD)	148 (STDEV ^(c) = 7)	~
Intrinsic permeability, k_0 (mD)	~	795 (STDEV ^(c) = 71)
Injection flow rate for rel. perm. test, $q_{methane}$ (ml/min)	8	8
Effective pore volume ^(d) , V_p (ml)	63.3	108.4
Statistical parameters	a (-)	0.816
	b (-)	14.714
	a ₁ (Pa)	14095
	b ₁ (-)	-0.242
Initial saturation of displacing fluid (methane), $S_{d,i}$ (-)	0	0

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Note: ^(a) (Dow, 1966); ^(b) (NIST, 2018); ^(c) standard deviation; ^(d) effective pore volume = nominal pore volume - hydrate volume.

Figure 1. Schematic of experimental setup (MPCC: multi-property characterization chamber, and LVDT: linear variable differential transformer).

Figure 2. Pressure-temperature (P-T) of HBS specimen ($S_h = 42.0\%$) during early warming-cooling process for specimen preparation and during relative permeability test. In the inset figure, black empty circles represent the P-T of specimen during early warming-cooling process, while the data in purple and red represent the P-T at inlet and outlet sides of specimen during relative permeability test, respectively.

Figure 3. Variation of differential pressure (ΔP) across specimen at different volumetric injection flow rates (q) during single-phase (brine) permeability measurements: R^2 -values of linear fittings (dashed lines) are > 0.990 .

Figure 4. Pressure-temperature (P-T) of HBS specimen ($S_h = 42.0\%$) and temperature of environmental chamber during relative permeability test.

Figure 5. Mass balance between methane injected into the specimen and methane vented from upper outlet port of sonic fluid separator during relative permeability test on HBS specimen ($S_h = 42.0\%$): The mass flow rate of vented methane is measured by the mass flow meter attached to the upper outlet port of sonic fluid separator (see Figure 1).

Figure 6. Differential pressure (ΔP) and accumulative volume of displaced brine (V_k) obtained during methane injection (at 8 ml/min) into (a) HBS specimen and (b) HFS specimen: The time is recorded from the onset of methane injection at the mass flow controller (MFC).

Figure 7. Trends of injected-to-displaced fluid volume ratio (V_i/V_k) and differential pressure across specimen (ΔP) vs. injected fluid-to-pore volume ratio (V_i/V_p) after break-through: **(a)** HBS specimen ($S_h = 42.0\%$) and **(b)** HFS specimen. Note that ΔP vs. V_i/V_p trend is plotted in log-log scale. The empirical constants of a , b , a_1 , and b_1 are to be utilized in the relative permeability calculation based on (Toth et al., 2002).

Figure 8. Relative permeability curves of (a) HBS specimen and (b) HFS specimen. Dotted lines represent the relative permeabilities extrapolated for 100 pore volumes (V_i/V_p) of methane injection.