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Authors

Wells, JD
Majid, AAA
Creek, JL
et al.

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1 **Water content of carbon dioxide at hydrate forming conditions**

2 Jonathan D. Wells^a, Ahmad A.A. Majid^{a,b}, Jefferson L. Creek^a, E. Dendy Sloan^a,
3 Sharon E. Borglin^c, Timothy J. Kneafsey^c, and Carolyn A. Koh^{a*}

4 ^aCenter for Hydrate Research, Chemical and Biological Engineering
5 Department, Colorado School of Mines, Golden, Colorado 80401, USA. Email:
6 ckoh@mines.edu

7 ^b Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia
8 Pahang, Malaysia

9 ^cLawrence Berkeley National Laboratory, 1 Cyclotron Rd, Berkeley, CA
10 94720, USA

11

12 **Abstract**

13 There is an interest to ensure sub-saturated water content in lines
14 containing carbon dioxide in applications such as enhanced oil recovery and
15 carbon sequestration, to reduce risks of hydrate blockage and corrosion. The
16 water content of carbon dioxide at various temperature and pressures has
17 been measured in the past, but there is no consistent set of measurements
18 that could be used for carbon dioxide storage and transportation design
19 work. The solubility of water in a carbon dioxide rich gas phase at hydrate
20 forming conditions was measured in this work. Pressures ranged from 12.06
21 to 29.30 bar along two isotherms, 1°C and -7°C, all within the gaseous

22 carbon dioxide and hydrate stability zone. For the first time in these types of
23 measurements, the solid phase was also characterized and confirmed to be
24 carbon dioxide hydrate via X-ray computed tomography, simultaneous with
25 water content measurements of the gas phase. Once carbon dioxide hydrate
26 conversion had reached a maximum value (65% estimated by X-ray
27 computed tomography), the equilibrium water content was measured. Prior
28 to reaching this maximum carbon dioxide hydrate conversion, the water
29 content in carbon dioxide was observed to decrease as liquid water
30 converted to carbon dioxide hydrate. This slow conversion to hydrate,
31 metastability of the hydrate phase, or unexpected phases may be
32 responsible for the large discrepancy between prior data sets for similar
33 carbon dioxide water content measurements.

34 **Keywords**

35 Carbon dioxide, clathrate hydrate, water content, metastability, X-ray
36 Computed Tomography

37 **1. Introduction**

38 Various applications, like enhanced oil recovery and carbon
39 sequestration, depend on flowing nearly pure carbon dioxide through lines.
40 With anthropogenic carbon emissions on the rise every year, there are lots of
41 efforts being made to remove carbon dioxide from the atmosphere before
42 irreversible damage is done.[1-4] While there are various techniques for
43 capturing carbon dioxide from the atmosphere into a concentrated stream so

44 that is may be sequestered, in nearly all of them carbon dioxide must be
45 transported from where it is captured to where it will be stored.[5-7] [8] In
46 particular for subsea applications, carbon dioxide will have to be transported
47 through the ocean at low temperatures and high pressures.[9,10] It is
48 important that these lines stay clear and maintain flow, as downtime is both
49 expensive and can pose safety concerns.[11]

50 Even in a nearly pure carbon dioxide stream, gas hydrate can form and
51 accumulate with very small (ppm) amounts of water in the line.[12] Gas
52 hydrates are ice-like crystalline compounds that form at the thermodynamic
53 conditions found in many gas pipelines, allowing hydrates to form in and
54 potentially block gas flow lines.[12] Hydrates are both costly to remove from
55 a line and also pose a large safety hazard for operation, so they must be
56 carefully managed or preferably avoided.[13,14] In gas transportation with
57 already low water content, like carbon dioxide, it is common to dry gas below
58 the water saturation pressure to avoid a free water phase and hydrate
59 formation.[15,16] In order for this drying scheme to work, the water content
60 of gas in equilibrium with hydrate must be accurately known so the gas may
61 be dried below this value to prevent any formation.

62 The carbon dioxide hydrate phase boundary is well understood. Initial
63 measurements began in the Donald L. Katz group in the 1940s[17] and have
64 continued with others up through 2000.[18-20] Values are well established
65 and in good agreement for the P-T location of the phase boundary. More
66 recent carbon dioxide hydrate data has been published, but mostly in gas

67 mixtures as applications like hydrate based separations and carbon
68 sequestration have received more focus.[21,22]

69 While P-T equilibrium measurements for hydrates are quite common,
70 very few studies consider the water content of the bulk gas phase. In
71 particular, for carbon dioxide, there are only a few data sets in the open
72 literature, many of which are in disagreement with one other as seen in
73 Figure 1.

74

75 Figure 1- Literature data for saturated water content in liquid carbon dioxide as a function of pressure.
76 Each linear fit represents an isotherm given next to line. Blue circles are from Wiltec²³, orange
77 diamonds are from Chapoy²⁰, and green triangles are from Song & Kobayashi¹⁹.

78 The Kobayashi group was one of the first to make these measurements
79 in 1986, utilizing a stirred autoclave equilibrium cell.[23] The liquid CO₂
80 phase water content data shows a strong, unexpected, function of pressure

81 for water content as seen by the triangles in Figure 1. Further data showing
82 this same trend was presented in a 2019 GPA Midstream technical report
83 from Song et al. [24] More recently in 2011, Chapoy et al. measured the
84 water content of carbon dioxide, and showed no dependence on pressure in
85 a static (non-flowing) cell with impeller mixing (diamonds in Figure 1).[25]
86 Similarly, data from Burgass et al., all collected below the ice point, show
87 almost no function of pressure in the liquid phase CO₂ water content
88 measurements.[26] In addition, other groups have made this measurement,
89 like the work done by Seo et al. and Youseff et al that do not show this
90 strong pressure dependence.[27,28] Most recently, two more groups in 2015
91 showed this same weak function of pressure, one using a static cell at Korea
92 University, and another in a flowing system at Wiltec (circles in Figure 1).[29]
93 In all of these experiments measuring water content over carbon dioxide
94 hydrate, only the gaseous or liquid carbon dioxide phase was ever evaluated.
95 None of these studies considered evaluating the solid phase to determine
96 whether it is hydrate, metastable hydrate, or metastable ice/liquid water.

97 Hydrate and ice metastability are both well documented phenomena.
98 [30–33] In particular, for carbon dioxide hydrate, Ripmeester's group
99 observed that ice can exist longer than 2 days at conditions where carbon
100 dioxide hydrate is the thermodynamically stable solid phase.[34]
101 Additionally, these different water phases (liquid, ice, or hydrate) may have
102 different vapor pressures. For this reason, it is important to ensure that the

103 solid phase is hydrate, while measuring the saturated water content of the
104 bulk carbon dioxide gas phase.

105 There are various analytical in-situ techniques for determining ice,
106 hydrate, or liquid water existence. For example, Raman spectrometry has
107 been successfully used in the past to discriminate between different hydrate
108 structures.[35] However, Raman measures conditions at a very small
109 sample spot (few microns) and the conventional method would be
110 challenging to also measure equilibria conditions during in a macroscopic
111 system. Conversely, X-ray computed tomography (CT) can distinguish
112 differences in densities within an entire system in a very short time.[36,37]
113 Density differences are large enough to differentiate phases during carbon
114 dioxide hydrate formation in the X-ray CT scanner. While water has a
115 specific gravity of 1, that of ice is slightly lower at 0.9, and for carbon dioxide
116 hydrate it is slightly higher at 1.1.[38]

117 In this work, the water content of carbon dioxide at hydrate forming
118 condition is measured, while the water phase is simultaneously characterized
119 in situ. Previous works have shown large discrepancies between reported
120 CO₂ water content values, and no work was performed to distinguish
121 between potential metastable solid phases. Differences in the water content
122 of CO₂ literature values may be due to the presence of a metastable liquid
123 water or ice phase instead of actual carbon dioxide hydrate. In addition to
124 making water content measurements, this work investigates the
125 metastability of water at hydrate forming conditions based on X-ray CT data

126 collected simultaneously with water content measurements, and high
127 pressure differential scanning calorimetry (HP-DSC) experiments to confirm
128 and quantify the formation of hydrate.

129 **2. Materials and Methods**

130 In all tests, deionized water was utilized to form the carbon dioxide
131 hydrate. Carbon dioxide was used as the hydrate guest molecule throughout
132 this work, at a purity of 99.9995% obtained from Airgas. The column packing
133 was made from chenille fabric (100% cotton), available off the shelf at any
134 fabric store.

135 2.1 Packed Column

136 In this study a packed column flowing apparatus was constructed to
137 make phase equilibrium measurements, similar to that used by Jasperson et
138 al.[29] Water content of the effluent carbon dioxide stream was monitored
139 via gas chromatography (GC) at Lawrence Berkeley National Laboratory
140 (LBNL) and gas chromatography mass spectrometry (GCMS) at the Colorado
141 School of Mines (CSM) to ensure steady state was achieved. This
142 continuously flowing setup eliminates much of the sampling difficulty present
143 in a static cell.

144 An overview of the apparatus is given in Figure 2. Pressure and
145 temperature were both measured at the inlet to the testing section. The key
146 section is the aluminum tubing in the center (1.27 cm ID x 45.72 cm long)
147 filled with the chenille packing. Carbon dioxide hydrate is assumed to form

148 only in this section, as it is the only place where water is present. The test
149 section is packed with chenille fabric to increase the surface area over which
150 carbon dioxide hydrate formation occurs. Chenille was used as packing
151 since it does not have a microporous structure that may prevent water from
152 converting to carbon dioxide hydrate, and it is X-ray transparent, as is the
153 aluminum used for tubing in the testing section. This trait was important to
154 be able to use the X-ray CT to quantify the water phase.

155 In most phase equilibria measurements, getting representative
156 samples at equilibrium conditions is a major challenge. For the work
157 performed at LBNL, an isolated section of tubing at the outlet was utilized to
158 obtain a sample of the outlet gas. After evacuating this section, it was filled
159 with a carbon dioxide gas sample from the effluent of the column and then
160 heated to 110°C. After heating, the sample section filled with the heated
161 carbon dioxide was then opened to a gas bag. Because the gas bag was
162 only partially filled, the pressure in the bag was atmospheric. From the gas
163 bag, a syringe was used to inject an aliquot of the sample onto a Shimadzu
164 GC-8A gas chromatograph (GC) with a Hayesep Q packed column and
165 thermal conductivity detector (TCD) to detect the water content of the
166 carbon dioxide gas.

Figure 2- Schematic of the packed column apparatus developed to measure phase equilibria at hydrate forming conditions. From gas bag, sample was injected into GC for water content analysis at LBNL or directly to GCMS (no bag) at CSM.

For the experiments performed at CSM, the equilibria apparatus and GCMS are in close proximity to each other, so a small (1.5875 mm) heated line from the outlet of the aluminum testing section directly to the GCMS was utilized instead of a gas bag. This small change ensures a representative equilibrium sample is being injected into the GC column and eases the sampling procedure. Analysis at CSM was done with an Agilent 6890 Gas Chromatograph with an Agilent 5973 Mass Selective Detector and pneumatic gas injection valve. Aside from the above, the VLE saturation columns used at LBNL and CSM are identical.

To operate the packed column, the chenille fabric was first saturated with water, then loaded into the tubing. Thermal equilibrium was then reached at 1°C before the system was pressurized to 29.3 bar with carbon

183 dioxide to achieve hydrate forming conditions. Pressure (Transamerica 0-
184 1500 psi transducer, 09384/CEC-1000-04) and temperature (Omega
185 Engineering Type T thermocouple, TMQSS-062U-18) conditions were then set
186 to the desired experimental values. To sample, the sampling section was
187 first evacuated via a vacuum pump (Hitachi 160VP Direct Drive Rotary
188 Vacuum) before being filled with sample and then heated to 110°C to ensure
189 the whole sample was vaporized and to prevent condensation of water on
190 tubing line. Finally, an aliquot of the collected sample was transferred to the
191 GC (or GCMS at CSM) for sampling via gas bag (or directly to the heated
192 sample line at CSM).

193 2.2 X-ray Computed Tomography (CT)

194 While measuring water content, the aluminum testing section was on
195 the table of a GE Lightspeed 16 medical CT scanner at LBNL with X-rays of
196 120 kV potential. X-ray CT allows three-dimensional density distributions to
197 be collected of the testing section while flowing CO₂ and measuring water
198 contents at the outlet. With knowledge on the different densities between
199 ice, liquid water, and carbon dioxide hydrate, the phases present inside the
200 testing section can be determined.[39,40] The resolution of densities
201 collected depends on the voxel size of 0.625 x 0.195 x 0.195 mm which
202 results in 550 slices per scan, which in all took 2 minutes to complete.

203 2.3 High Pressure Differential Scanning Calorimetry (HP-DSC)

204 A Setaram μ -DSC VIIa micro-differential scanning calorimeter was
205 utilized to measure water conversion to carbon dioxide hydrate. The HP-DSC
206 has a maximum pressure of 154 bar and operating temperature of -45 to 120
207 °C. In the work, measurements began by loading 1 cm x 1 cm section of
208 chenille fabric (same as column packing) into the cell. ~15 mg of water was
209 then added onto the fabric. To form carbon dioxide hydrate, the sample was
210 pressurized to the test condition (29.3 bar), and then cooled to 1 °C at a rate
211 of 0.5 °C /min. The temperature was held at 1 °C for various times (16, 24,
212 42 hrs) to evaluate the amount of carbon dioxide hydrate formed at different
213 times. The temperature was increased slowly at a rate of 0.1 °C /min up to
214 room temperature after an initial hold period to melt the carbon dioxide
215 hydrate crystals so that the conversion could be evaluated.

216

217 **3. Results and Discussion**

218 3.1 Water Content Measurements

219 Carbon dioxide hydrate was first formed with the greatest driving force
220 (highest pressure on a given isotherm), and then the pressure was
221 isothermally lowered in order to collect water content data on water content
222 of the CO₂ gas and hydrate formation data as a function of time and
223 pressure. X-ray CT scans were taken approximately every 2 hours during the
224 day and water content was measured immediately after each scan. Once
225 the X-ray CT scans showed no further carbon dioxide hydrate formation and

226 the water content measurements remained constant, that water content was
227 reported as the final equilibrium concentration.

228 Since the gas – hydrate region of the carbon dioxide and water phase
229 diagram is not very large, only 2 isotherms were acquired to represent the
230 region: one at 1°C and another at -7°C. Carbon dioxide hydrate was
231 nucleated and annealed at 1°C before moving to the experimental
232 temperature for both isotherms. This temperature gives the largest driving
233 force for carbon dioxide hydrate formation, while remaining above the ice
234 point. It was desirable to stay above the ice point as hydrate formation
235 kinetics are much faster when forming from liquid water compared to ice.
236 The results for both isotherms and corresponding Multiflash 6.2 Cubic Plus
237 Association (CPA) predictions are shown in Figure 3- Equilibrium water
238 content of gaseous carbon dioxide at hydrate conditions collected along 2
239 different isotherms (1 (orange) and -7°C (blue)) compared with predicted
240 values from Multiflash CPA modelFigure 3.[41] The Multiflash CPA model
241 combines the Soave Redlich Kwong equation of state with further terms for
242 hydrogen bonding, making it a preferred model for gas hydrate equilibrium
243 predictions.[42]

Figure 3- Equilibrium water content of gaseous carbon dioxide at hydrate conditions collected along 2 different isotherms (1 (orange) and -7°C (blue)) compared with predicted values from Multiflash CPA model with hydrate phase. Error bars represent one standard deviation from 5 replicate experiments.

Both measured isotherms show a small decrease in water concentration with pressure. The higher temperature, 1°C, shows higher water contents in the gas phase compared to the lower temperature, as expected. Vapor pressure over solids increases with increasing temperature as molecules have more kinetic energy to escape into the gas phase. Measured values are close to predicted values from Multiflash CPA and even within error (one standard deviation of 5 replicate experiments) for most points. Other phase equilibrium software designed for forecasting hydrate formation and phase properties, like in-house software CSMGEM[43] (stands for Colorado School of Mines, Gibbs Energy Minimization), was evaluated and found to match Multiflash predictions almost exactly. To verify that the tube had sufficient residence time to reach equilibrium at 0.1 mL/min, the flow

260 rate was doubled (to 0.2 mL/min) and CO₂ water contents were measured.

261 Water content values at the higher flowrate were within error of those

262 measured at the original flowrate (0.1 mL/min).

263 Figure 4 compares the data collected in this work to previously
264 measured values for gaseous carbon dioxide water content. Note the limited
265 amount of data for this system; far more data is available at conditions
266 where carbon dioxide exists as a liquid.

267

268 *Figure 4- Comparison of measured water content (labeled CSM) in gaseous carbon dioxide (grey and*
269 *green circles) to previous data collected by Youssef (orange diamonds) and Song et al (blue triangles)*
270 *plotted on a log-inverse scale. Error bars on CSM data represent one standard deviation from 5*
271 *replicates and are almost smaller than the points.*

272 The data collected in this work (error bars are one standard deviation
273 from 5 replicates) are in agreement with water contents measured
274 previously in other labs for similar pressures. On a plot of natural logarithm
275 of concentration of water versus inverse absolute temperature plot, the data
276 are all linear, as predicted by the Clausius-Clapeyron equation for a

277 univariant system.[44] Note that the Clausius-Clapeyron equation, normally
278 applied to a pure component, applies equally well to this binary, but
279 univariant system.

280 The data do indicate a weak function of pressure, as may be expected
281 with a highly compressible gas phase. The highest pressure data (at CSM
282 24.1 bar) falls at the lowest water content compared to the other lower
283 pressure at the corresponding temperature. While collecting the equilibrium
284 values, X-ray CT was utilized to ensure that all liquid water had converted to
285 carbon dioxide hydrate.

286 3.2 Effect of bulk water phase

287 While measuring the water content of carbon dioxide, CT scans were
288 being taken at the same times. CT scanners work by measuring densities
289 inside of each voxel in the system. Liquid water, ice, and carbon dioxide
290 hydrate densities differ enough for them to be detected in the scanner. In
291 this analysis, changes in density from initial conditions (liquid water and
292 carbon dioxide gas) were evaluated. At the beginning of the experiment, a
293 scan of the packing saturated with water was taken at ambient conditions.
294 Then, after cooling and pressurization, further scans were taken and
295 differences between each condition and the initial water system were taken.
296 Colors have been assigned to the values for density differences to make
297 viewing easier in ImageJ.[45,46] A sample of this can be seen with the CT
298 scan in Figure 5.

Figure 5- (top) X-ray CT scan taken 2 hours after hydrate nucleation and (bottom) X-ray CT scan taken 16 hours after hydrate nucleation at 1°C and 29.3 bar. Red represents a density increase (carbon dioxide hydrate), white is no change, and blue is a density decrease, all relative to the starting liquid water conditions (1.27 cm ID x 45.72 cm long).

This scan was taken two hours after carbon dioxide hydrate nucleation occurred and is a cross section down the center of the pipe. These scans are only differences in density between the scan taken at each time and the initial scan with liquid water. CO₂ entered the tube on the right had side, flowing to the outlet at the left at 0.1 mL/min. The tube walls can be seen at both the top and bottom of each image. Red represents an increase in density, blue represents a decrease, and white is no change. Increases in density indicate hydrate formation since carbon dioxide hydrate is denser than the original liquid water. Density decreases are due to liquid water vacating its position to move towards the carbon dioxide hydrate and being replaced by gas. Ice would be shown in Figure 5 by a lighter blue color compared to the deep blue of a liquid moving away and being replaced by a gas (larger density change). Since the differences are being taken from liquid water, white represents positions where density has not changed and liquid water still exists. It can be seen in the scan at two hours (Figure 5 top)

323 that there is some carbon dioxide hydrate formation on the right side, which
324 is where carbon dioxide flowed into the system. There is still a significant
325 amount of unconverted water (white) further downstream.

326 At longer times, like 16 hours after nucleation, further carbon dioxide
327 hydrate formation has occurred. The area of red (carbon dioxide hydrate)
328 has spread much further downstream (to the left) and less liquid water
329 (white) remains, as seen in the bottom portion of Figure 5. There are still
330 some white regions which contain liquid water that may be converted to
331 carbon dioxide hydrate.

332 Finally, after 46 hours, the tube has become nearly all red due to
333 carbon dioxide hydrate formation (Figure 6, top). There is almost no liquid
334 water remaining. This can be confirmed by changing the point of reference
335 to a later scan, at 42 hours. Because the subtraction is done at a new
336 reference point, it is nearly all white, indicating no changes in density have
337 occurred in those additional 4 hours. The constant density over this new
338 time frame indicates no more carbon dioxide hydrate has formed. Both of
339 these images can be seen in Figure 6.

340

341

Figure 6- Top: carbon dioxide hydrate formation (in red) 46 hours after nucleation at 1°C and 29.3 bar.
Bottom: Additional carbon dioxide hydrate formation from 42 to 46 hours after nucleation at 1°C and
29.3 bar. White indicates no further hydrate formation.

Further, the number of red/blue/white voxels can be quantified to be sure that nothing is changing between these two times. In Figure 7, the numbers of positive, negative, and zero valued pixels along the slice down the center of the tube were quantified for select times after nucleation with error from the standard deviation of 10 different axial slices of CT images. The plots in Figure 7 agree with what was seen in Figures 5-6, where major conversion occurs early (first 24 hrs) in the experiment, as can be seen by the sharp increase in positive density changes initially. For carbon dioxide hydrate to form, water must be consumed, as indicated by the decreasing number of zero value pixels. All of these values are constant by 42 hours after nucleation, which is consistent with the visual analysis shown in prior Figures 5-6.

Figure 7- Changes of X-ray CT density of pixels along centerline of tube at various times after nucleation. Error bars represent one standard deviation from 10 different axial slices of the CT images.

When each X-ray CT scan was acquired, the water content in the CO₂ gas effluent was also measured. In this way, the effect of carbon dioxide hydrate versus liquid water was evaluated. The water content of carbon dioxide decreased over time as liquid water converted to carbon dioxide hydrate, as seen in Figure 8. Error bars on this plot represent one standard deviation of 5 replicate experiments. The first point is likely high due to a higher measured temperature in the cell from the exothermic hydrate reaction. This temporary increased temperature from hydrate formation would also increase the measured water content. However, the temperature returns to the setpoint value (1°C) within 2 hours and any increased water content values after that are unlikely to be due to temperature effects. While the water content slowly decreased over the first 24 hours as liquid water converted to carbon dioxide hydrate, it finally reached a constant value once carbon dioxide hydrate conversion had completed. The phase of the water

375 in contact with the CO₂ is very important for these measurements, as it can
376 change the water content by nearly 50%. For this reason, the solid phase
377 must be evaluated when making hydrate equilibrium measurements.

378

379 *Figure 8- Water content of carbon dioxide over water (left side) and hydrate (right side) as liquid water*
380 *converts to hydrate over time at 1°C and 29.3 bar. X-ray CT scans confirmed maximum carbon*
381 *dioxide hydrate conversion after 40 hours. Dashed line represents Multiflash 6.2 CPA prediction (292*
382 *ppm,mol). Error bars represent one standard deviation of 5 replicate experiments.*

383 3.3 Carbon dioxide hydrate metastability

384 In addition to the X-ray CT, HP-DSC was performed to confirm water
385 metastability in the carbon dioxide hydrate forming region. Procedures for
386 these experiments were similar to those done previously at CSM, with the
387 exception that chenille fabric was added to the cell in order to increase
388 surface area to improve hydrate conversion and mimic the experimental
389 conditions in the X-ray CT. Conversion can be calculated based on the area

390 under the curve of the hydrate dissociation peak and knowledge of initial
391 water amounts.[47]

392 Using this technique, conversion was calculated after various
393 annealing times, which are summarized in Table 1 below. Additionally,
394 conversion in the X-ray CT apparatus was estimated from the CT density
395 values, like previously presented by Seol et al.[48] To calculate the
396 conversion, the average change in density for every slice was calculated
397 using ImageJ.[46] Next, the density change for each slice was converted to a
398 mass with knowledge of the voxel size. The total mass increase was then
399 summed, and with knowledge of the initial mass of water loaded into the
400 tube and ratio of water to carbon dioxide in hydrates, the conversion can be
401 calculated.

402 *Table 1- Calculated carbon dioxide hydrate conversion from differential scanning calorimetry*
403 *experiments and estimated conversion from X-ray CT data.*

Time after Nucleation (hrs)	HP-DSC actual conversion ($\pm 5\%$)	X-ray CT estimated conversion ($\pm 5\%$)
4	No formation	23%
16	47%	39%
24	55%	64%
42	54%	65%

404

405 Similar duration experiments were necessary to achieve maximum
406 conversion in both methods. Just like X-ray CT results, no further conversion

407 was seen after 24 hours in the HP-DSC. It was expected that hydrate
408 formation in both of these apparatuses would match well, as both utilized the
409 same packing materials and thermodynamic conditions. While the HP-DSC is
410 a quiescent system, the flow through the tube in the X-ray CT was low
411 enough that it was similar to the HP-DSC in terms of conversion timescales.
412 The actual conversion is slightly higher in the X-ray CT due to the increased
413 mass transfer from the flowing system. Due to the flowing nature of the X-
414 ray CT experiments, the conversion can never reach 100% since some water
415 (~300ppm level) is constantly flowing out of the system in the effluent
416 carbon dioxide stream during experiments.

417 Both the X-ray CT and HP-DSC experiments eventually became mass
418 transfer limited. There is no flow or mixing in the HP-DSC so once the water
419 at the interface converts to carbon dioxide hydrate, the remaining liquid
420 water inside the carbon dioxide hydrate shell will take much longer to
421 convert to hydrate because mass transfer through the hydrate shell is slow.
422 Similarly, the X-ray CT indicates a carbon dioxide hydrate shell forming even
423 with a low flow rate. The carbon dioxide hydrate forms at the edge of the
424 packing as seen in the area marked "Unconverted water in center) in Figure
425 5. The red (hydrate) at the edge of the fabric surrounds white (unconverted
426 water) as a carbon dioxide hydrate shell forms around the unconverted
427 water, slowing mass transfer and stopping any further hydrate formation.
428 Once this shell is thick enough that it prevents any further water conversion
429 to carbon dioxide hydrate, the gas outside the shell in the vapor phase is in

430 equilibrium with the carbon dioxide hydrate shell as seen by the constant
431 water content.

432 **4. Conclusions**

433 When measuring water content of gases at hydrate forming conditions,
434 it is important to not just characterize the phase in equilibrium with hydrates;
435 the solid phase (hydrate and metastable phases) must be also considered.
436 For the first time, water contents of gases at hydrate forming conditions
437 were measured while simultaneously the state of the water phase present in
438 the equilibrium. Specifically, two isotherms (1°C and -7°C) were collected
439 between 12.06 and 29.30 bar for gaseous carbon dioxide water content in
440 equilibrium with carbon dioxide hydrate. In order to verify values were
441 collected in equilibrium with carbon dioxide hydrate, X-ray CT was used to
442 simultaneously evaluate the state of the water phase. Initially, when liquid
443 water still persisted in the system and carbon dioxide hydrate conversion
444 was low, measured water content values were up to 50% higher than final
445 equilibrium values. As time moved forward and further liquid water was
446 converted to carbon dioxide hydrate, the water content of the CO₂ decreased
447 asymptotically until reaching equilibrium values as the gas came into
448 equilibrium with only a hydrate shell.

449 Water metastability within the carbon dioxide hydrate forming region
450 was also evaluated. X-ray CT indicated that carbon dioxide hydrate took
451 over 42 hours to achieve maximum conversion from liquid water at 29.3 bar

452 and 1°C. HP-DSC confirmed metastability results in the X-ray CT, as
453 conversion in two independent apparatuses took place over similar
454 timescales (>24 hours). Carbon dioxide hydrate conversion took so long
455 (>24 hours) in both systems due to the large amounts of water and mass
456 transfer limitations after maximum conversion. Water metastability is an
457 important parameter that must be considered when making hydrate phase
458 equilibrium measurements, as different water phases may lead to
459 significantly different measured water content in the equilibrated fluid phase.

460 **5. Conflicts of Interest**

461 There are no conflicts of interest to declare.

462 **6. Acknowledgements**

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466 Stadick and Mike Klasner were essential for getting the systems at CSM
467 working properly.

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