Supporting Information

for

Gas Hydrates Phase Equilibria and Formation from High Concentration NaCl Brines up to 200 MPa

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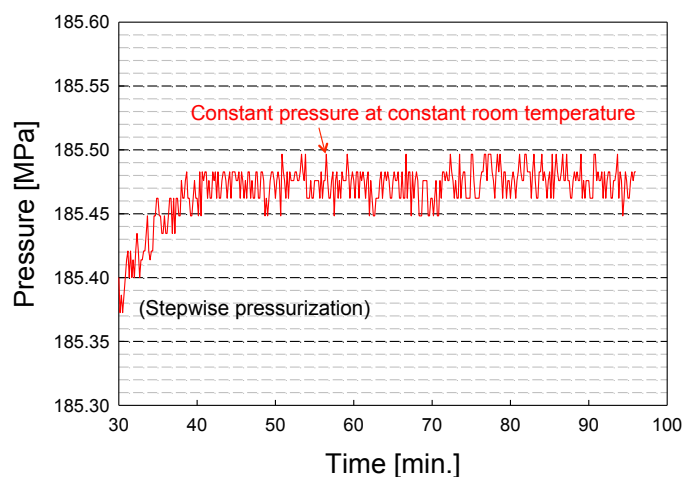[3]ConocoPhillips, Production Assurance, Bartlesville, OK, 74004 – USA

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1. HAZOP (Hazard and operability) Study for High Pressure Apparatus

The experimental setup (Fig. 3 in the manuscript) was manufactured for the measurement of hydrate phase equilibrium and formation kinetics in high salinity system and very high pressure. For safety considerations, a hazard and operability (HAZOP) study for the system was done based on the worst what-if scenario in terms of pressure/temperature/explosive issues.

- What if all gas pressurized in the system vents to the room?
- What if there is an emergency situation?
- What if hydrates plug a line during an experiment?
- What if all chiller temperature increases over the safety set value?
- What if the electrical power shuts down?

Fig. S1 Pressure test at around 186 MPa (~27,000 psi) with nitrogen gas.
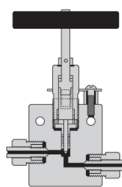
Ultra-High Pressure Cell in CSM

Top-Lid

Baffle (Made of Inconel)

Sample cylinder
(Made of Inconel)

Top view of UHP cell

Tubing

High Pressure Tubing 316 SS (HIP-30-9H2)
Pressure rating = 30,000 psig
Outer diameter = 1/8 inch, Inner diameter = 0.04 inch

Valves

High Pressure Valve
316 SS (HIP-60-HF2)
Pressure rating =
60,000 psig

Pressure Measurement

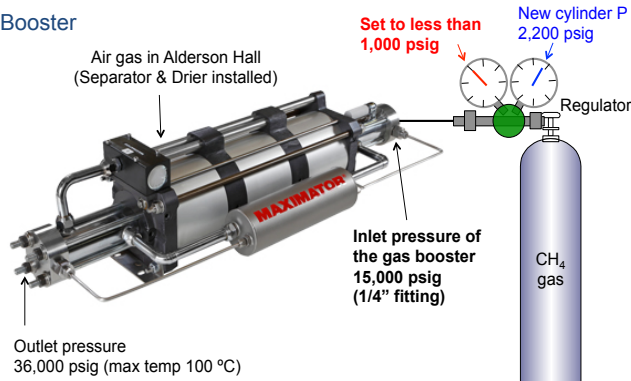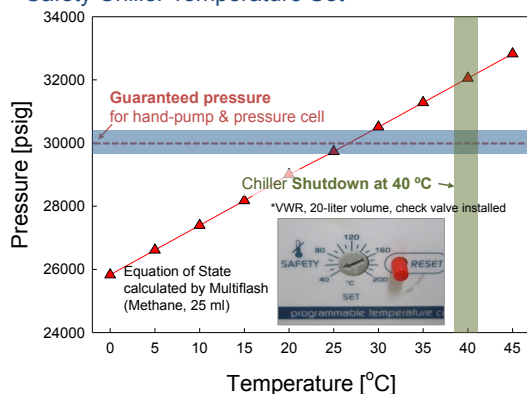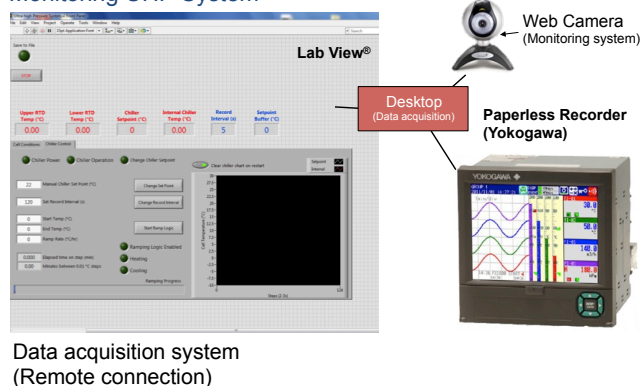Analogue   Digital   Transducer

Gas Booster

Air gas in Alderson Hall
(Separator & Drier installed)

Set to less than 1,000 psig

New cylinder P 2,200 psig

Regulator

Inlet pressure of the gas booster 15,000 psig (1/4" fitting)

CH$_4$ gas

Outlet pressure
36,000 psig (max temp 100 ºC)

Safety Chiller Temperature Set

Guaranteed pressure
for hand-pump & pressure cell

Chiller **Shutdown at 40 ºC** →

*VWR, 20-liter volume, check valve installed

Equation of State
calculated by Multiflash
(Methane, 25 ml)

Monitoring UHP System

Lab View®

Web Camera
(Monitoring system)

Desktop
(Data acquisition)

**Paperless Recorder
(Yokogawa)**

Data acquisition system
(Remote connection)

Safety Shield (Double Polycarbonate Plates Installed)

Frame   Frame

Polycarbonate

Reference: http://www.hoffmanonline.com

	METALS					NON-METALLICS				FINISHES		
Material	Mild Steel	304 SS	316 SS	Aluminum Die Cast	Aluminum Sheet	Poly-carbonate	Fiberglass'	Fiberglass''	Polyester	ABS	Powder Coat	Plated	Exotic Finish
Impact Resistance	3	2	②2	1	1	④4	3	3	5	4			

* Rating: 1 = Low, 5 = High

Polycarbonate

Pressure Relief Valve

316 SS (HIP-402633-30)
Pressure adjusted
30,000 psig (by Factory)

Length: 0.6"
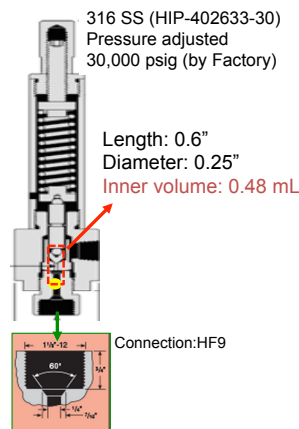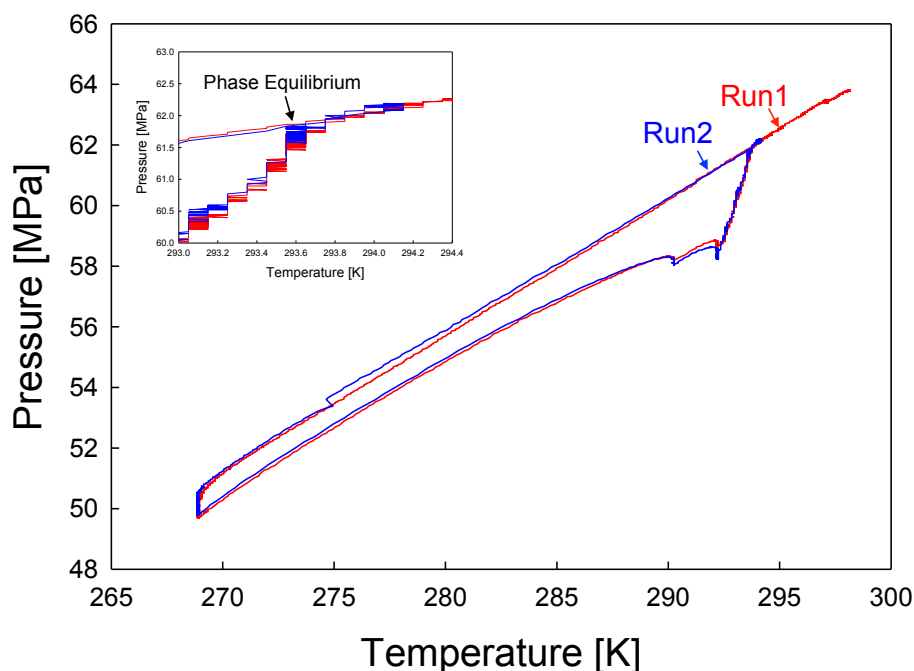Diameter: 0.25"
Inner volume: 0.48 mL

Connection:HF9

Fig. S2 Development of the high pressure system with various HAZOP considerations.

2. Reproducibility in Measurements of Hdrate Phase Equilibrium

All measurements of hydrate phase equilibrium were repeated with a fresh solution to check the accuracy and reproducibility.

Fig. S3 Temperature and pressure trace in repeat experiments for the measurement of hydrate phase equilibrium with 12 wt% NaCl system.

3. Methane Hydrate Phase Equilibrium Data Measured

Table S1 Measured experimental data points for methane hydrate phase equilibria with NaCl. Gray colored rows are data points measured in repeat experiments.

Salinity	Phase Equilibrium Measured	
	Temperature (K)	Pressure (MPa)
Pure Water	295.75	34.3
	305.75	103.7
	301.65	69.3
	307.45	122.1
	309.85	150.1
	311.95	177.7
12 wt.% NaCl	288.00	29.1
	290.41	37.8
	290.44	37.8
	293.75	62.0
	293.55	62.0
	296.29	80.7
	298.55	102.8
	298.45	102.6

	301.95	142.1
	304.65	183.9
23 wt.% NaCl	277.45	28.0
	278.26	32.0
	278.35	32.0
	282.25	56.9
	284.75	78.3
	287.35	99.5
	290.85	145.5
	293.25	183.4
26 wt.% NaCl	278.85	62.0
	278.75	62.0
	282.55	97.1
	285.55	132.2
	288.65	182.5
27 wt.% NaCl	279.45	77.8
	282.55	113.5
	286.05	172.7
30 wt.% NaCl	279.55	78.1
	284.45	141. 4

4. Equations for Measurements of Formation Rate / Conversion Ratio / Salt Precipitation

Calculations of water conversion to hydrate and amount of salt precipitated during hydrate formation are based on following assumptions:

- Methane gas is immiscible in water. The amount of gas dissolved in water is relative small compared the total volume of gas phase in the cell.
- The solubility of sodium chloride (NaCl) in water is independent of pressure.
- The calculation does not consider the degree of supersaturation during the experiments.
- The volume change from water to hydrate is neglected.

(i) Formation rate: The number of moles of gas consumed at a given time t can be calculated through following equation:

$$\left(\Delta n_{gas}\right)_t = V_{tot}\left[\left(\frac{P}{zRT}\right)_{t=0} - \left(\frac{P}{zRT}\right)_t\right] = \frac{V_{tot}}{v_{t=0}} - \frac{V_{tot}}{v_t} \tag{1}$$

where $(\Delta n_{gas})_t$ is the number of moles of gas consumed to form the hydrate at time t. z and v represents the compressibility factor and molar volume, respectively, at temperature, T, and pressure, P in the pressure cell at given time t, which are calculated with an equation of state. V_{tot} is the total volume of gas phase in pressure cell and tubing, which is assumed to be 32.28 mL. R is the universal gas constant.

(ii) Conversion from water to hydrate: percentage of amount of water consumed to form hydrate over total amount of water in the system can be determined by

$$\text{conversion from water to hydrate}\,(\%) = \frac{\left(\Delta n_{gas}\right)_t \times \text{hydration number}}{n_{water}} \times 100 \tag{2}$$

where hydration number used in this study is 6. n_{water} is the total number of moles of water in the system.

(iii) Sodium Chloride (NaCl) precipitation: The amount of salt precipitated is calculated by

$$\text{NaCl Precipitation} = m_{salt} - \frac{\left[n_{water} - \left(\Delta n_{gas} \right)_t \times \text{hydration number} \right] \times M_w \times c_{saturation}}{1 - c_{saturation}} \quad (3)$$

where M_w and n_{water} represent the molecular weight of water and initial number of moles of water in the system, respectively. The saturation concentration of NaCl in aqueous solutions at 5.5 °C ($c_{saturation}$) is assumed to be 0.263 in this study. m_{salt} is the total amount of salt in the system.

5. Calculation of Conversion from Water to Hydrate
Once hydrate starts to form, the gas will be trapped in the hydrate cavities and system pressure will decrease. Take the system with 26 wt.% NaCl as an example.
(1) Volume of gas phase in the system

Table S2. The total volume of system includes both volume of cell and fitting parts.

Total Volume		Liquid Phase Volume	Gas Phase Volume
Cell Volume	Fitting Volume		
56 cm^3	1 cm^3	25 cm^3	32 cm^3

(2) Formation rate

Table S3. The amount of hydrate formed is determined from the difference between the initial and final cell pressure and temperature.

	Initial	Final
V_{tot}	32 cm^3	32 cm^3
t	0 hr	18 hr
P	151.6 MPa	135.0 MPa
T	288.15 K	278.75 K
v (predicted from EOS)	39.4725 cm^3/mol	40.0167 cm^3/mol
n	0.8107 mol	0.7997 mol
$(\Delta n_{gas})_t$	0.0110 mol	

(3) Conversion from water to hydrate

Table S4. The conversion to hydrates is estimated by an equation of state assumed hydration number of 6.

$(\Delta n_{gas})_t$ gas occupied in hydrate	Water consumed to form hydrate		Initial n_{Water} prepared	% Hydrate
	n Hydration number	$n_{water,H}$ Water formed hydrate		
0.0110 mol	6	0.0660 mol	1.2387 mol	5.3 %

6. Calculation of Sodium Chloride (NaCl) Precipitation

(1) Formation rate

Table S5. The amount of hydrate formed is determined from the difference between the initial and final cell pressure and temperature.

*After first inflection point $t_{1\ after}$

	Initial	Final
V_{tot}	32 cm^3	32 cm^3
t	0 hr	3.2 hr *
P	151.6 MPa	152.0 MPa
T	288.15 K	278.85 K
v (predicted by EOS)	39.4725 cm^3/mol	39.8097 m^3/mol
n	0.8107 mol	0.8038 mol
$(\Delta n_{gas})_t$	6.8667×10^{-3} mol	

(2) Amount of water in liquid phase

Table S6. The conversion to hydrates is estimated by an equation of state assuming a hydration number of 6. The water in the liquid phase is consumed to form the hydrates, resulting in the decrease of water in solution.

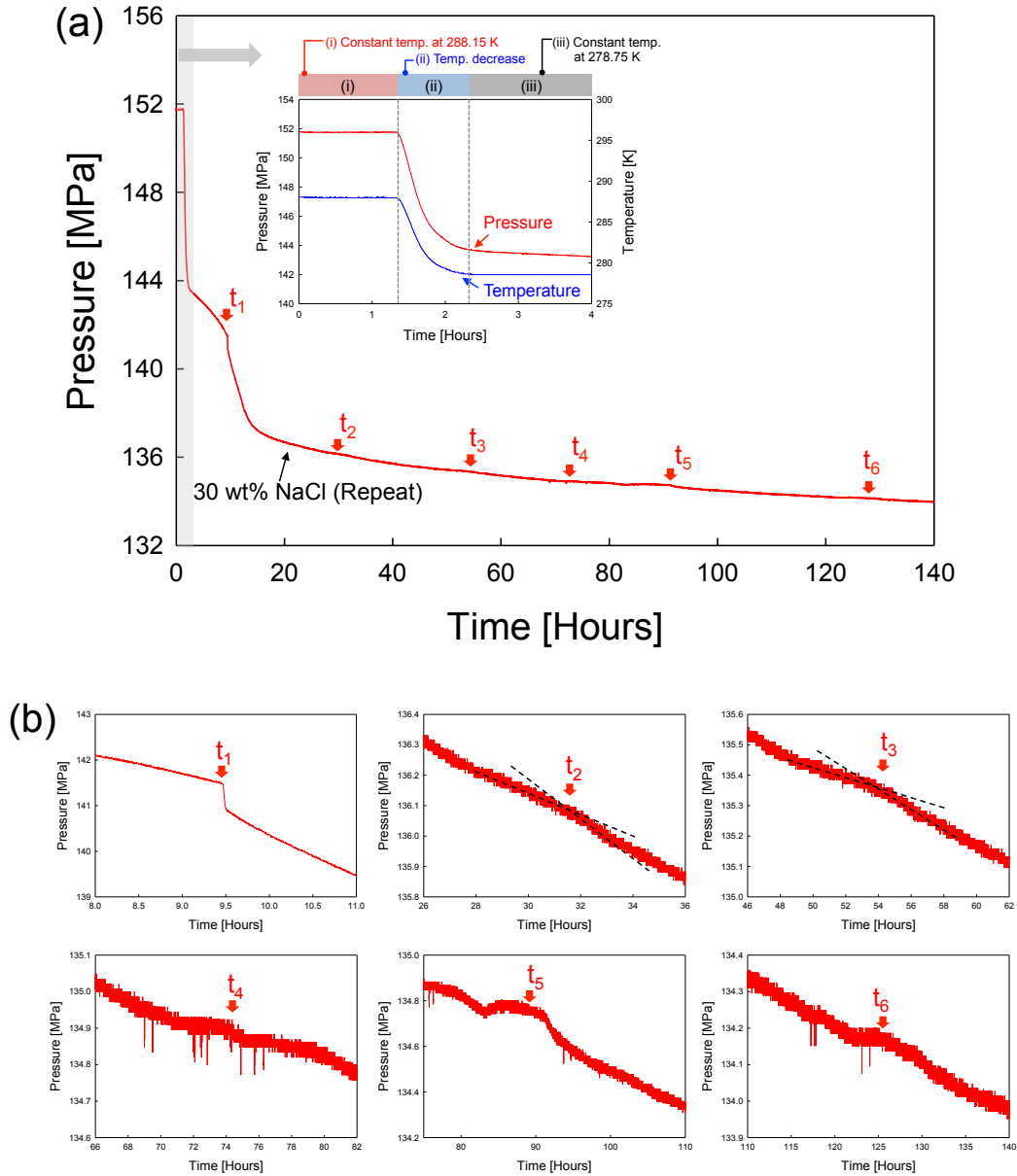| $(\Delta n_{gas})_t$ Gas occupied in hydrate	Water consumed to form hydrate		Initial n_{Water} prepared	Water in liquid phase	
	n Hydration number	$m_{water,H}$ Water formed hydrate		M_w	$m_{water,L}$ Water in liquid
6.8667×10^{-3} mol	6	0.0412 mol	1.2387 mol	18 g/mol	21.5550 g

(3) Amount of salt precipitation

Table S7. As the amount of water in the liquid phase decrease with constant saturation concentration at 288.15 K, the salt will precipitate out from the solution.

Initial m_{salt} prepared	Salt in solution			Salt Precipitation
	$m_{water,L}$ Water in liquid phase	$C_{saturation}$ Saturation concentration	$m_{salt,L}$ Salt in solution	
7.8338 g	21.5550 g	26.3 wt%	7.6919 mol	0.1419 g

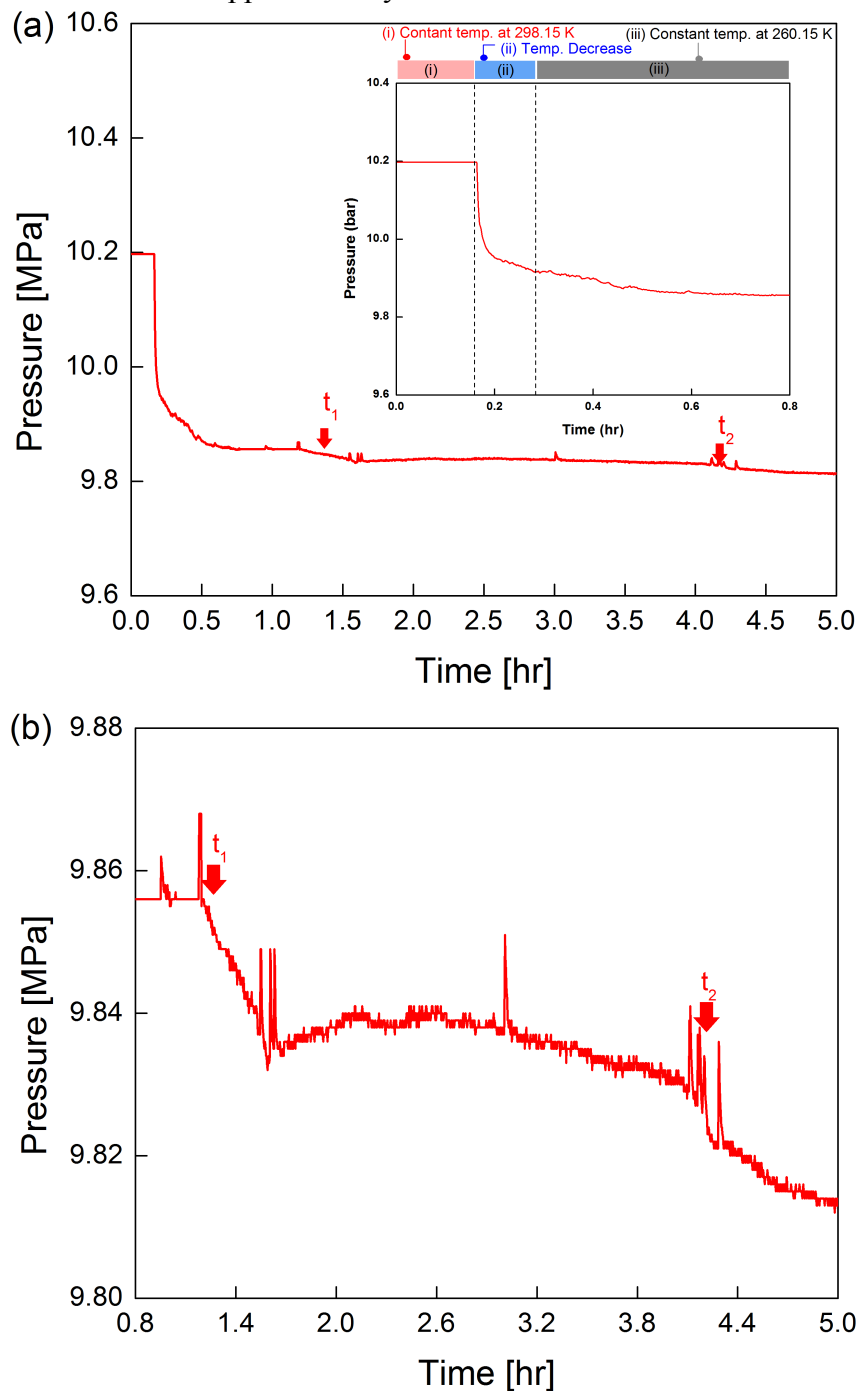## 7. Kinetic (Hydrate Formation Rate) Experiments in 30 wt% NaCl System

Inflection points during kinetic experiments always occurred in high salinity system as shown in figure below. This supports the competition for solid precipitation (salt or hydrates).

Fig. S4 Measurements of growth rate for methane hydrates in 30 wt% NaCl system. (a) hydrate formation rates in 30 wt% NaCl system: (i) started experiment at 288.15 K and around 152 MPa, (ii) decreased cell temperature and (iii) maintained at 278.75 K. (b) some inflection points occurred at time of t_1 to t_6.

8. Kinetic (Hydrate Formation Rate) Experiments in 27 wt% NaCl System

Inflection points are also observed in the experiment with 27 wt% NaCl, conducted in an autoclave cell with windows at approximately 10 MPa and 260.15 K with methane gas.
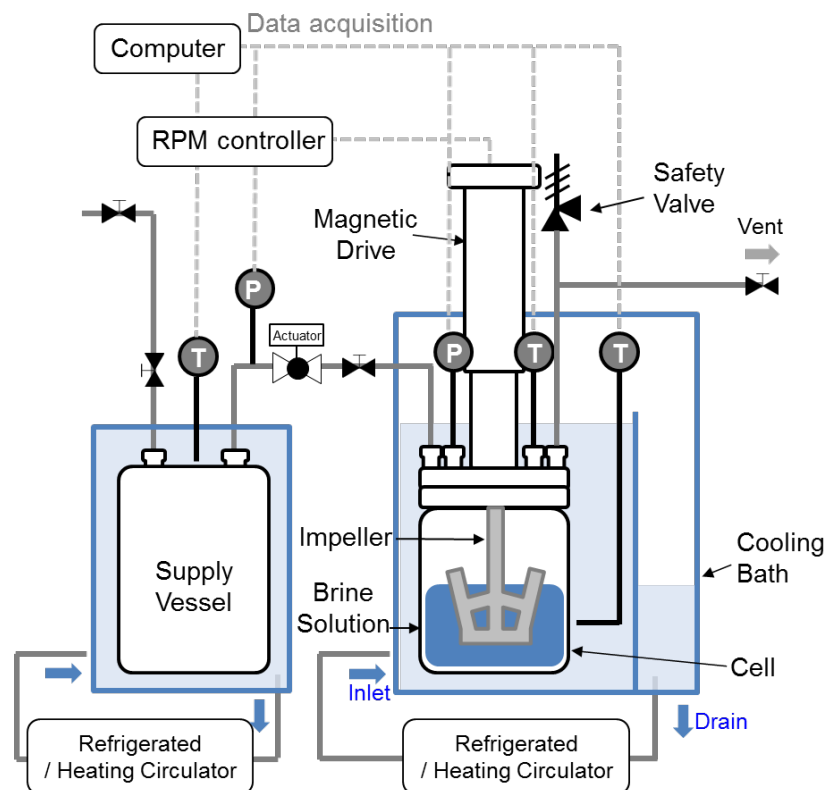

Fig. S5 Measurements of growth rate for methane hydrates in 27 wt% NaCl system. (a) Hydrate formation rates in 27 wt% NaCl system: (i) started experiment at 298.15 K and around 10.2 MPa, (ii) decreased cell temperature and (iii) maintained at 260.15 K. (b) Some inflection points occurred at time of t_1 and t_2.
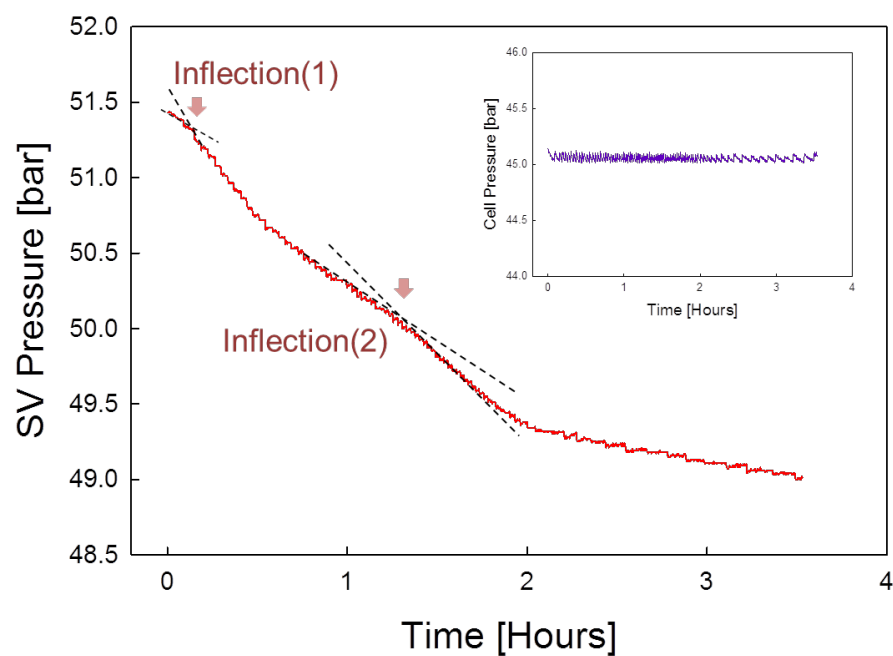
9. Kinetic (Hydrate Formation Rate) Experiments in 30 wt% NaCl System

Inflection points, corresponding to sudden pressure drop, are also detected in the experiment performed at 4.5 MPa and 258.15 K through the apparatus shown in Figure S6. The variations of pressures in the supply vessel (SV) and cell with time are included in Figure S7. During hydrate formation in the experiment, the gas was sent from the supply vessel to the cell through the actuator valve to keep a constant cell pressure, as shown in the inset in Figure S7, and as such, the pressure trace of supply vessel in Figure S7 indicates the amount of gas trapped in the hydrates and demonstrate the competing effects of solids (hydrates and salts) through the observed inflection points.

Fig. S6 Experimental apparatus used for kinetics experiments in 30 wt% NaCl system.

Fig. S7 Measurements of growth rate for methane hydrates in 30 wt% NaCl system performed at 4.5 MPa and 258.15 K. Two inflection points are observed on the supply vessel (SV) pressure trace. The inset shows the pressure in the cell, which is maintained at 4.5 MPa.