Understanding Gas Hydrates and its Utility for Energy Solutions

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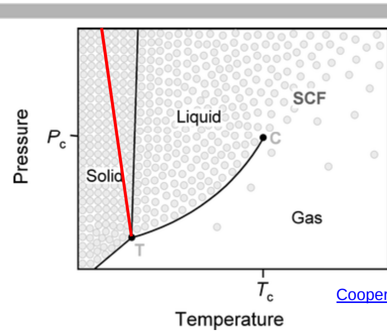
Gas hydrates are ice like crystalline material and they shares some of the unique properties of water

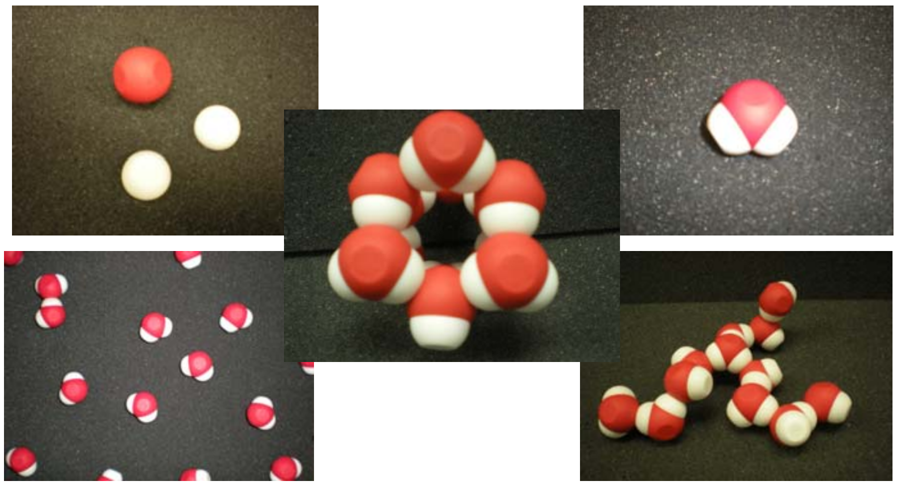


Cooper, A.I., *J. Mater. Chem.*, 2000, **10**, 207-234

- Density of solid water (ice) is lower than liquid water and this is one reason why life exist of earth.
- Water molecules have very different boiling point compared to other molecule of similar molecular weight.
- Within the solid ice phase, 13 known phases of ice has been identified

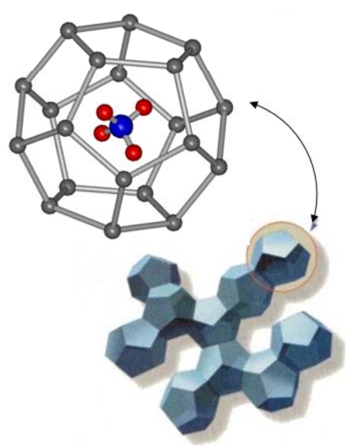
Molecular structure of water in different phases

Photographs are from Janda Lab

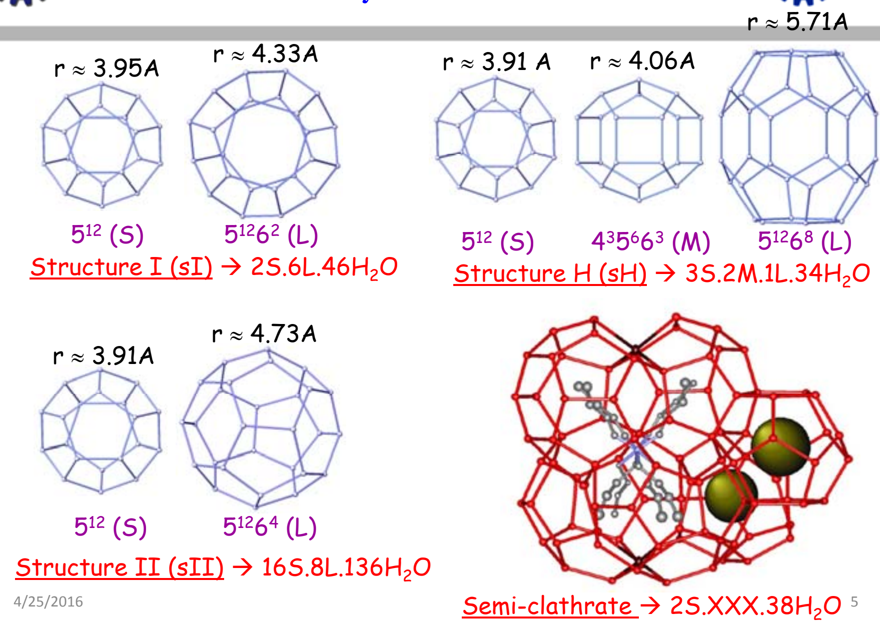


Gas hydrates are ice like crystalline material

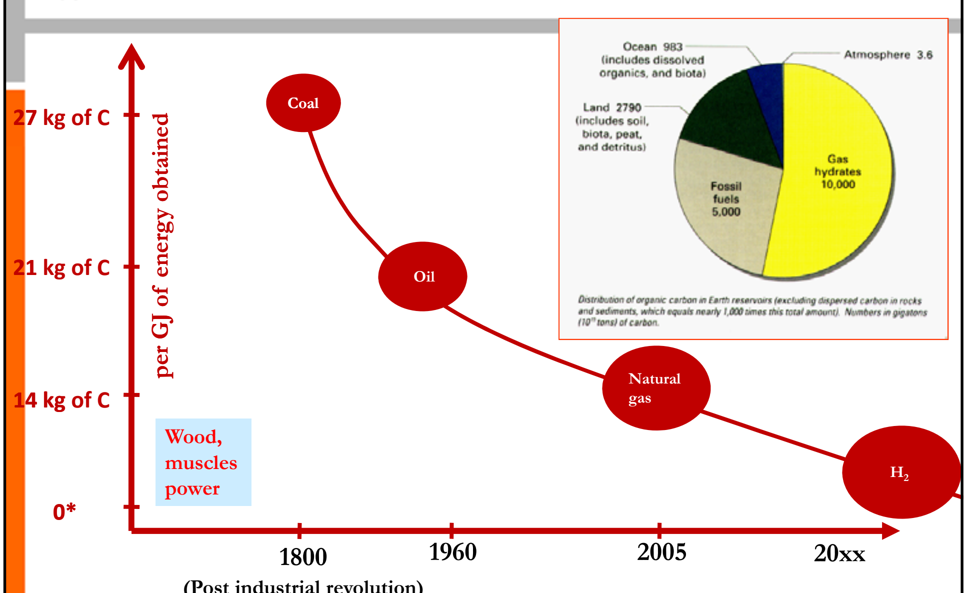
- Gas hydrates are crystalline non-stoichiometric compounds consisting of water and natural gas (CO_2, CH_4 etc.) physically resembling ice.
- Hydrogen bonded water molecules (host) create a cage that encloses a guest molecule (typically small molecules like H_2, CO_2, CH_4, neo-hexane)
- In nature gas hydrates are frequently encountered under sub sea environment (due to native high pressure and low temperature environment)



Different guest size results in different hydrate structure



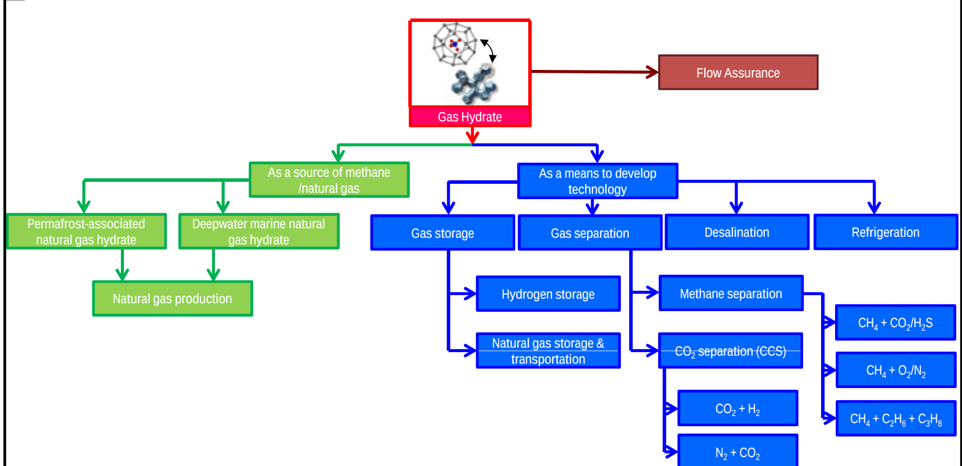
Importance of Natural Gas for Energy Solutions



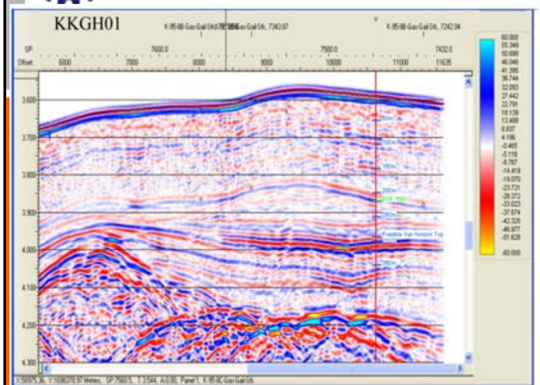
Clathrate Hydrates in Nature

- Natural gas is a mixture of mainly methane (90-99%), ethane (0-10%), propane (0-6%) & CO_2 (0-5%) etc.
- Both pure methane and natural gas hydrates exist in the natural world (not only on earth but also on other planets)
- Large quantity of methane hydrate exist on earth either in permafrost or under the sea bed along continental margin
- Gas hydrates are a good energy resource but it can also be a potential geo hazard.
- Methane is 21 times more potent green house gas than CO_2 and due to rise in global warming, methane in natural hydrates can decompose and create runaway effect

Why Study Clathrate Hydrate



Gas hydrates are found below permafrost or the ocean floor



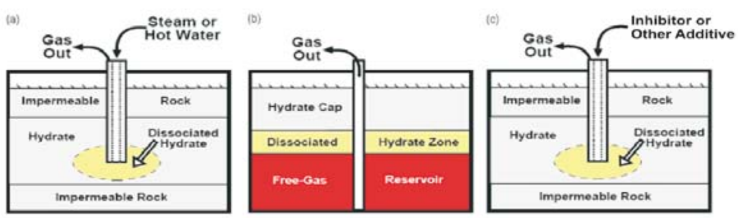
A hydrate glacier sits on the sea floor, 850 m below the surface*

http://communications.uvic.ca/releases/mr020909ph.html

- Total Conventional NG: 300 – 370 TCM (around the world)
- NGH estimates worldwide: ~ 20,000 TCM (mean estimate)
- NGH estimates in India: ~2000 TCM (NGHP estimate)
  - Even if 10 % is recoverable ➔ 200 TCM
  - World consumption of Natural Gas per year = 2.4 TCM

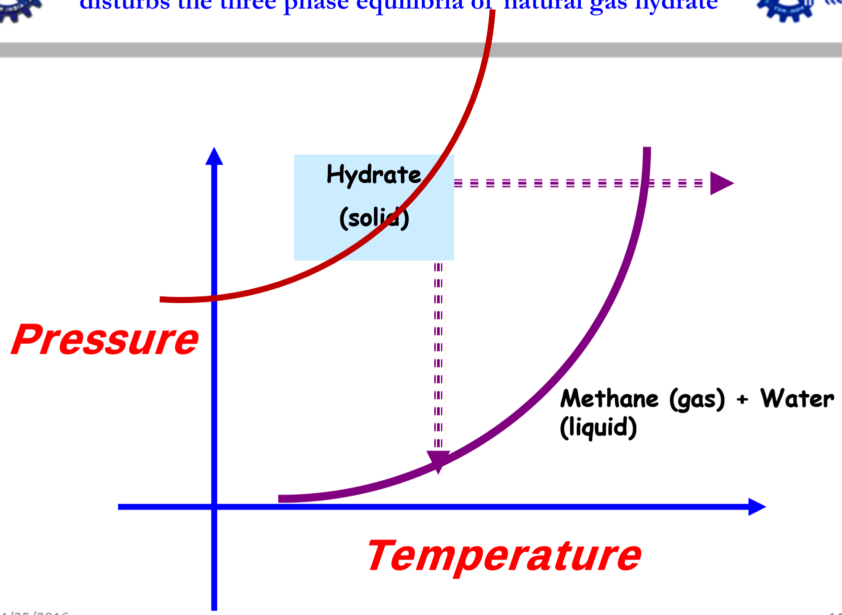
Proposed GH exploitation techniques

(adapted from Collett, 2002).

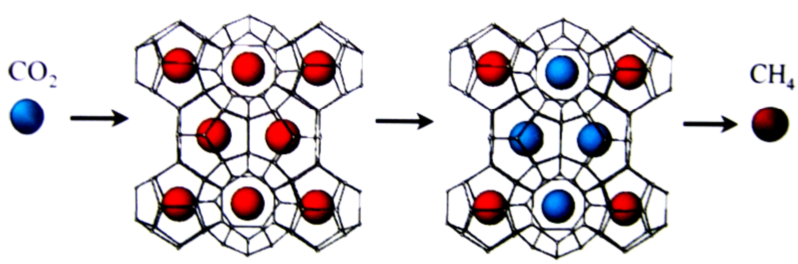


(a) thermal injection,
(b) depressurization,
(c) inhibitor or other additive

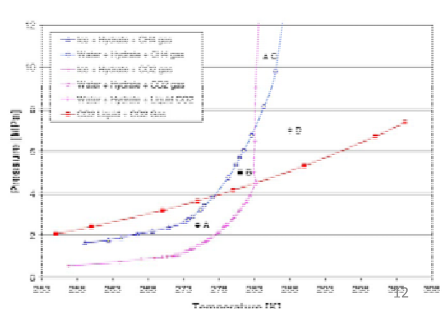
Pressure reduction, thermal stimulation or additive addition disturbs the three phase equilibria of natural gas hydrate



Sustainable production of methane by molecular replacement

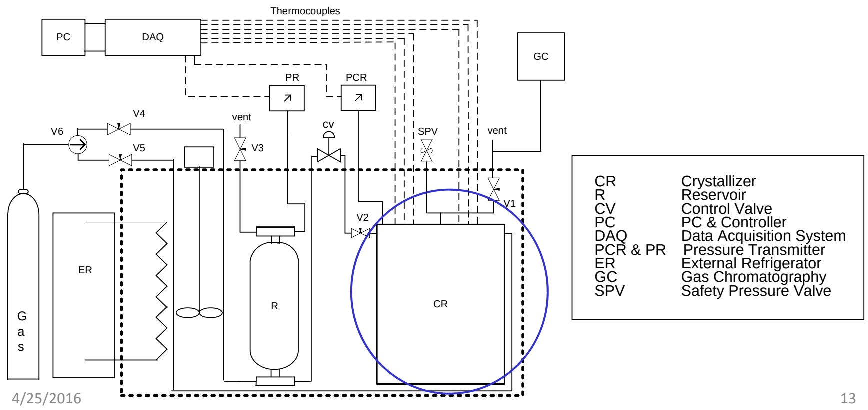


- Thermodynamic feasibility
- Kinetics of replacement
- Structure stability & Thermodynamic stability

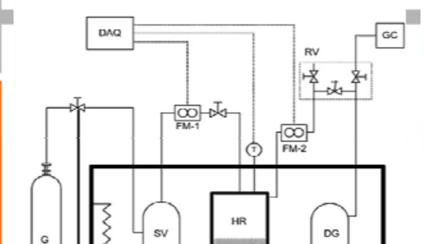


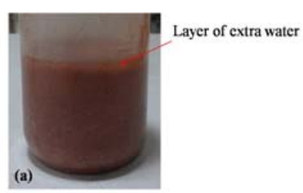
Schematic of the experimental setup

The current setup has been designed and built with a design pressure of 15 MPa, and temperature range between -15 and 60°C. This setup can study methane hydrate dissociation in a wide range of conditions; like water depth of up to 1500 meters, and typical soil overburdens with different methane hydrate saturations.



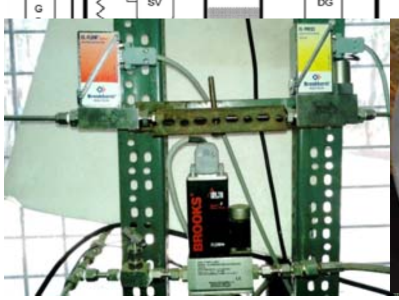
A set of mass flow meter and pressure controllers simultaneously simulates the marine environment in lab scale setup





Over saturated silica sand

Removal of extra water in a measuring cylinder




Temperature and pressure controlled high pressure setup for gas hydrate studies
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Bench Scale High Pressure Continuous Setup
4/25/2016
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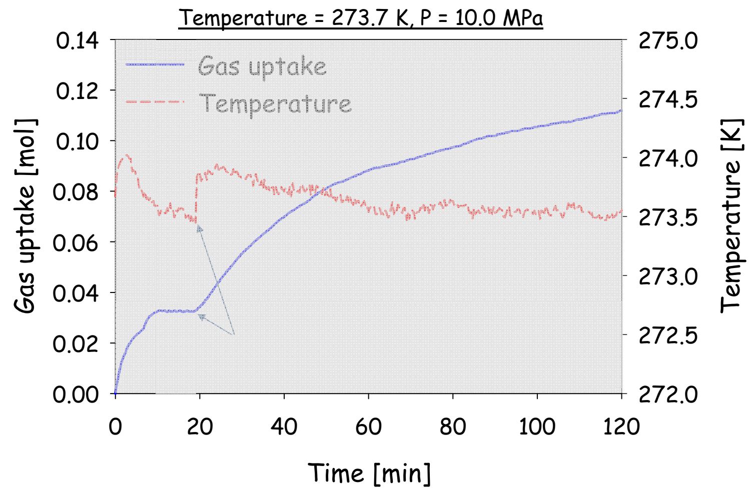
Typical gas uptake curve for hydrate formation



Chemical Engineering Science, 62, 4268-4276 , 2007

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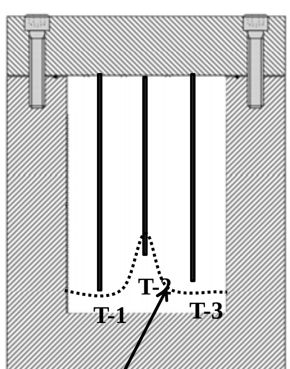
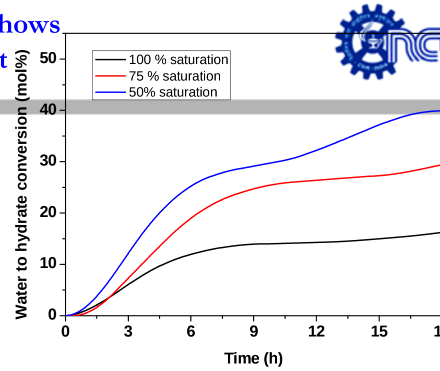
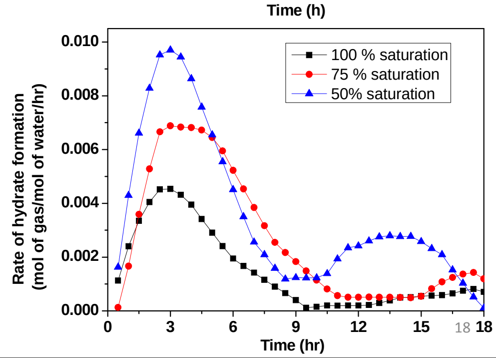
Hydrate formation kinetics shows multiple nucleation event



Cooling / Heating Coil





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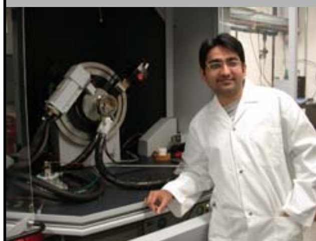
Conclusion from lab scale measurements

- Methane recovery through thermal stimulation alone is possible
  - Kinetics of hydrate decomposition is lumped kinetics
- Decomposition of methane hydrate and its recovery by depressurization alone (without any thermal stimulation) does not self sustain.
  - In absence of thermal stimulation partial recovery of methane is obtained at slower kinetics
- CH_4 recovery by CO_2 replacement is technically feasible, however focus should not only be on the kinetics of methane replacement but also on overall methane recovery
  - Still the question remains, what is the mechanism for such replacement? And what drives the replacement ?

Understanding gas hydrate & methane recovery at molecular level

- Understanding the structure and cage dynamics of gas hydrates through state of the art analytical tools
- Understanding molecular level replacement kinetics through molecular dynamics simulation of hydrate formation and decomposition.

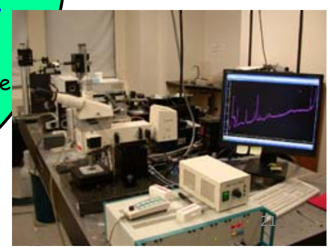
Understanding gas hydrate at molecular level through state of the art analytical tools: measurement on solid hydrate phase



Solid state NMR
T_{min}= -120°C
P_{max}= ~ few MPa
Quantitative technique for Cage occupancy

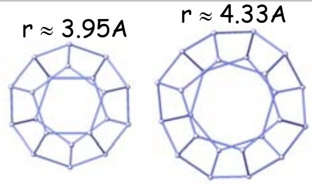
X-ray Diffraction
T_{min}= -150°C
P_{max}~ few MPa (rare)
Structure determination

Raman Spectroscopy
T_{min}= -190°C
P_{max}~ few GPa
Qualitative technique for Cage occupancy



Different guest size results in different hydrate structure

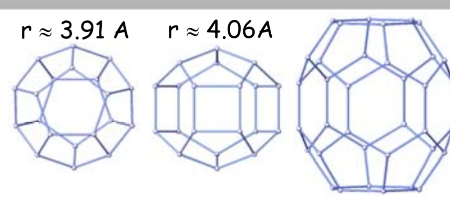
r ≈ 3.95A   r ≈ 4.33A



5^{12} (S) $5^{12}6^2$ (L)

Structure I (sI) → $2S.6L.46H_2O$

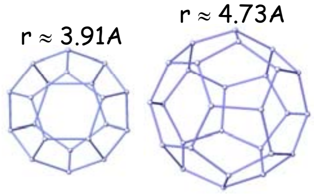
r ≈ 3.91 A   r ≈ 4.06A   r ≈ 5.71A



5^{12} (S) $4^35^66^3$ (M) $5^{12}6^8$ (L)

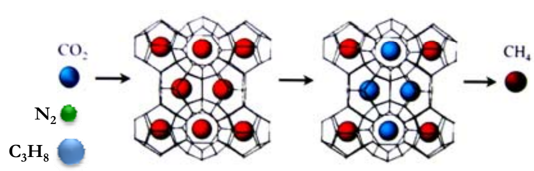
Structure H (sH) → $3S.2M.1L.34H_2O$

r ≈ 3.91A   r ≈ 4.73A

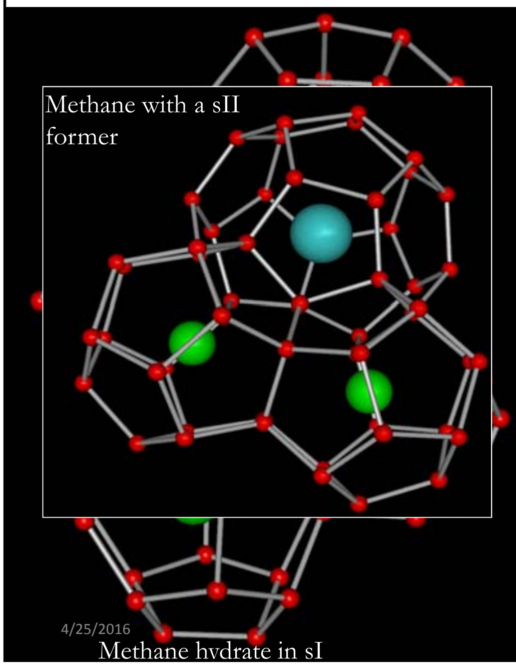


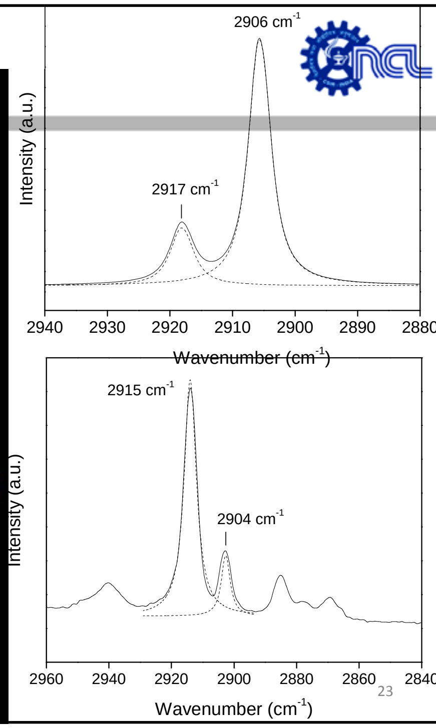
5^{12} (S) $5^{12}6^4$ (L)

Structure II (sII) → $16S.8L.136H_2O$



Large to small cage ratio in SI is 3:1, and in SII is 1:2





Distribution of natural gas in the hydrate phase

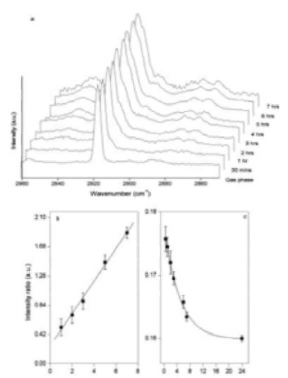


Figure 11. *In situ* Raman spectra of the C—H region for $CH_4/C_2H_6/C_3H_8$ hydrates obtained at 268 K and 2.8 MPa.

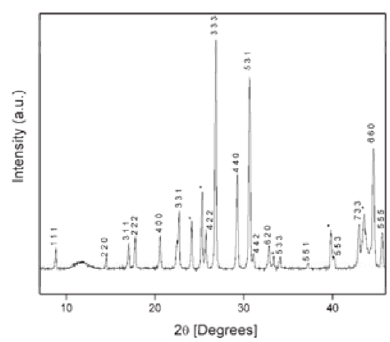


Figure 7. PXRD pattern of sII hydrate performed at 163 K on hydrate sample synthesized by $CH_4/C_2H_6/C_3H_8$ mixture at 2.8 MPa and 270 K.

AIChE J. 54,2132-2144, 2008.

Calculation of cage occupancy through Raman and NMR Spectroscopy

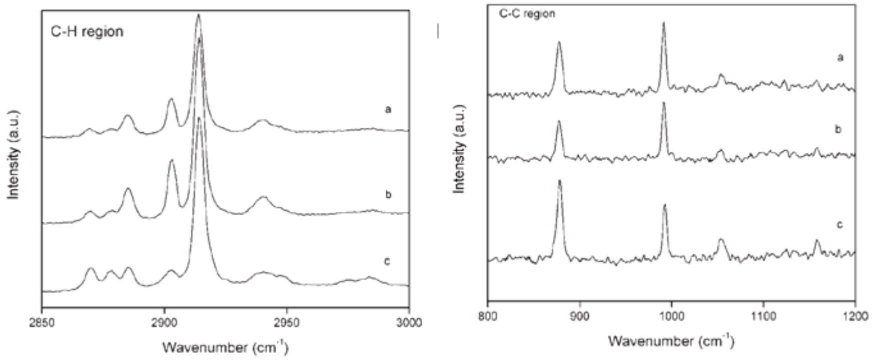
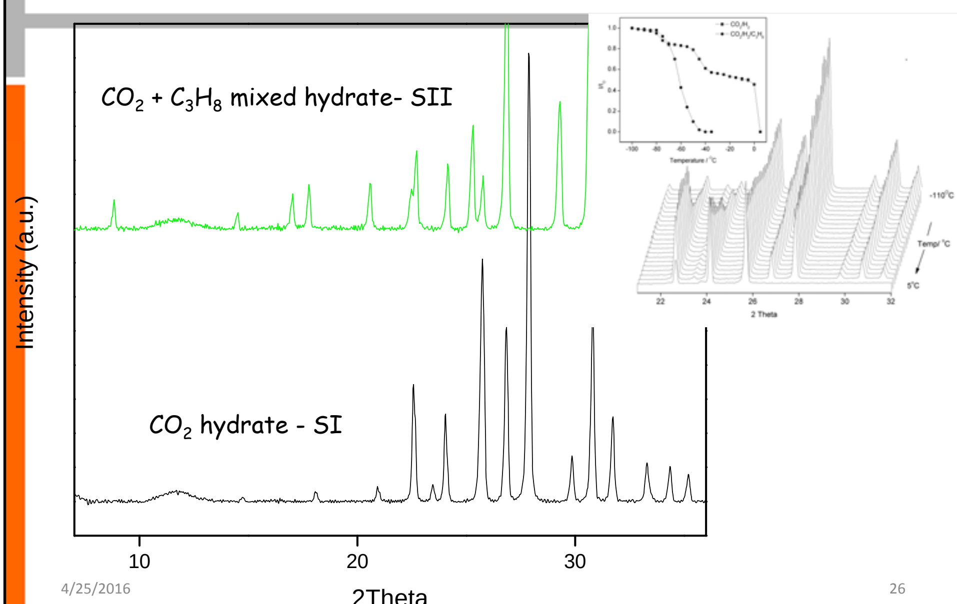


Table 8. Cage Occupancy Values Obtained by Combination of Results from Raman & Gas Chromatography, Which Compares Well with Results Obtained with ^{13}C MAS NMR

Description	Hydrate Structure	Methane θ_S	Methane θ_L	Ethane θ_L	Propane θ_L	Hydration Number n
Raman + gas chromatography (mole balance calculation)	sII	0.893	0.236	0.450	0.314	6.10
C^{13} NMR, high power decoupling (statistical thermodynamic model)	sII	0.888	0.287	0.446	0.264	6.13

Kumar et al. AIChE, 2008

Long term kinetic stability of resultant hydrate



Understanding methane recovery at molecular level through MD simulation

- All atomistic molecular dynamics simulations can give
  - intrinsic kinetics of hydrate decomposition
  - One such simulation has identified a unique decomposition pattern
- MD will help in identifying the methane replacement mechanism in presence of CO_2 and other small gases (nitrogen is a potential candidate) for better methane recovery.
  - CO_2-N_2 mixture is important because flue gas from thermal power stations also needs to be sequestrated
- MD simulation can help design and speed test additives which can be screened before carrying out an expensive experimentation in the lab.
  - We have tested few additives in gas phase and few in liquid phase

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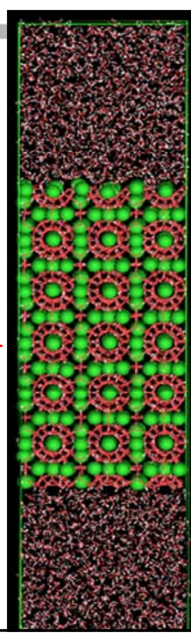
MD Simulations points toward a layer by layer decomposition

Bulk Water

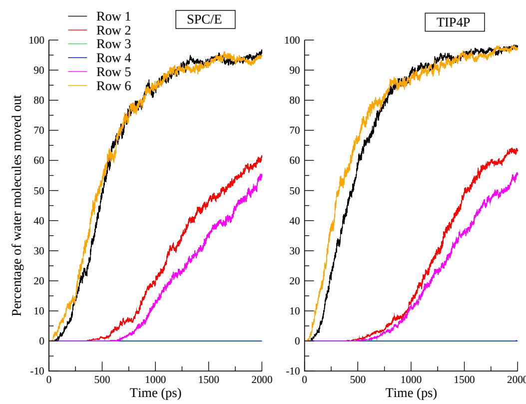
Hydrate Cages (3 x 3 x 6 unit cells)

Z
Y
X

Bulk Water



100 bar



The Journal of Physical Chemistry C, 117, **2013**, 12172-12182

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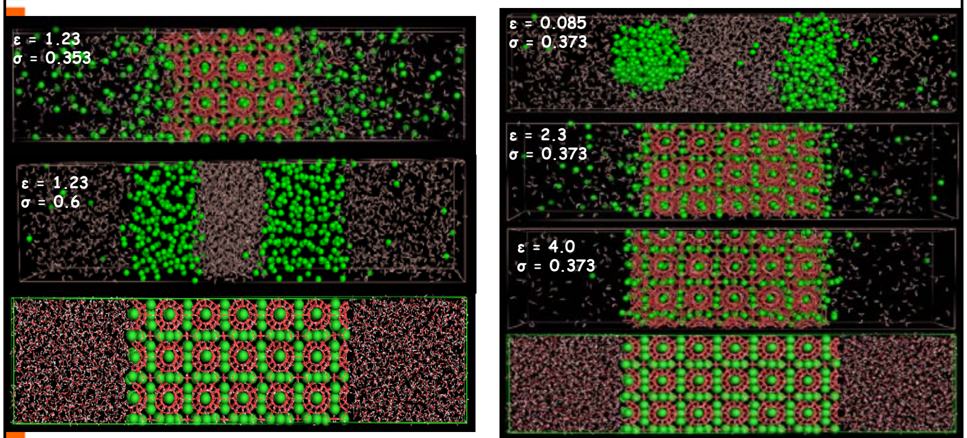
Evaluation of optimum gas molecule which can replace methane in natural gas hydrate: MD Simulations



ε in KJ/mol; σ in nm; Snap shots were taken after 2ns of run time

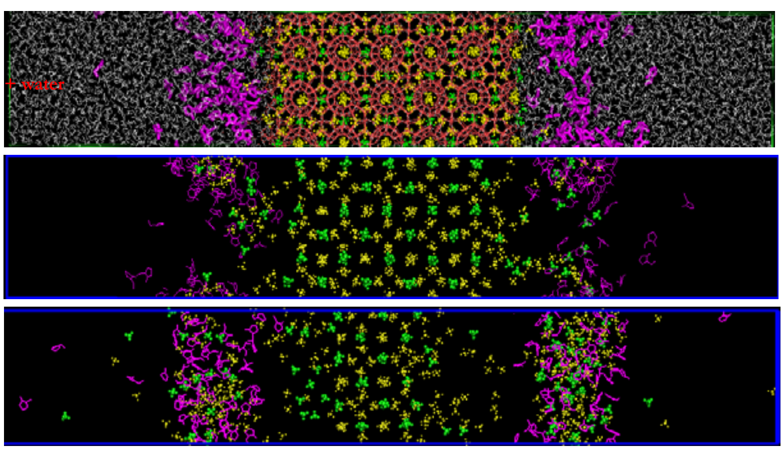
4/25/2016 *Physical Chemistry Chemical Physics*, 2015, **17**, 9509-9518 29

Additive design and validation: MD and Experimentation

Additive + water

500 ps

2000 ps



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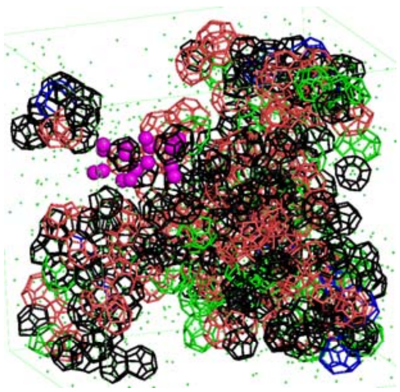
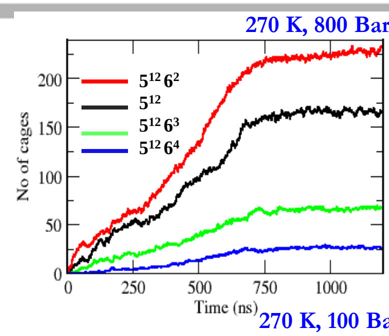
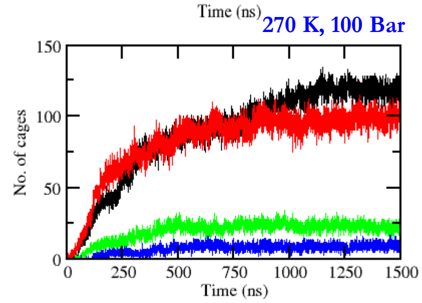
Methane hydrate formation kinetics



Black 5^{12}
Red $5^{12}6^{2}$
Green $5^{12}6^{3}$
Blue $5^{12}6^{4}$

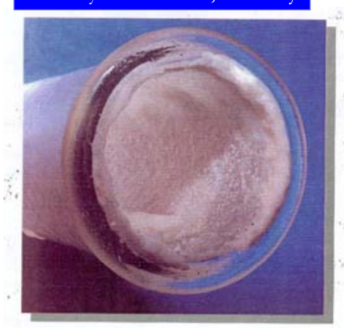




Gas hydrate formation in oil and gas pipelines: A nuisance

Hydrates may stick on pipeline walls.. and block flow

Courtesy of **SINTEF**, Norway



Hydrate deposition on a pipe wall

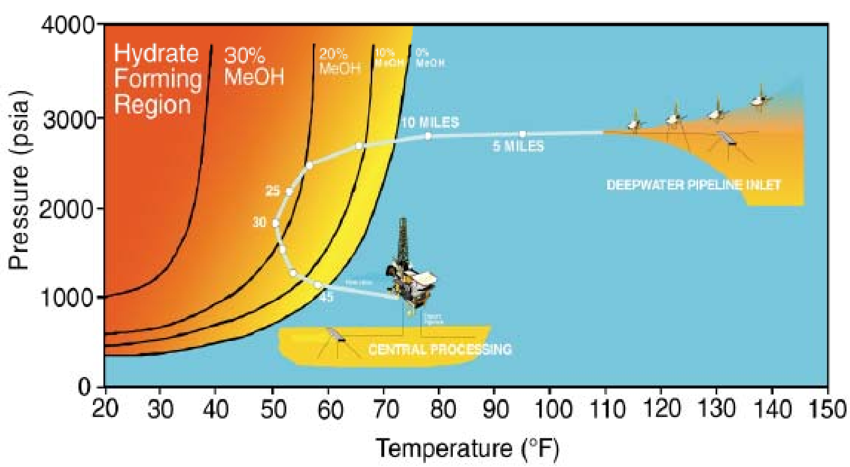
Deadly accidents and plant damages from improper hydrate plug removal in the order of millions of $$

Hydrate plugs move with high velocity (300 km/hr)

Cost at one oil field: $10 million/day

3

Thermodynamic inhibitors has limited applicability



C. Koh, *Chem Soc Rev* 2002 *31* 157-167

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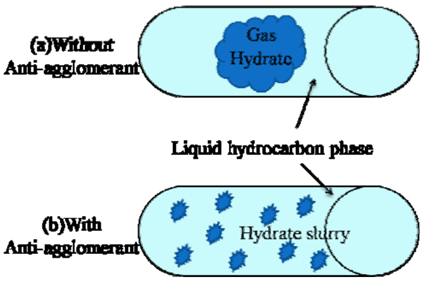
KHI can be more cost effective at higher water cut

•Development and test of crystal inhibitor with two key properties

•Inhibition of crystal nucleation and inhibition of crystal growth

•Control of nucleation in proteins, inhibition of urinary stone formation, inhibition of ice formation in living tissues during cryo-protection, control of crystal size in ice creams



Moving from production at 300m sea depth to production at 2000m.

(courtesy STATOIL, Norway)

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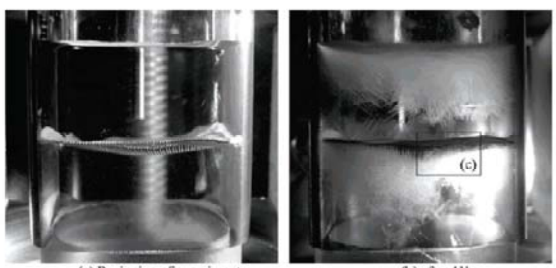
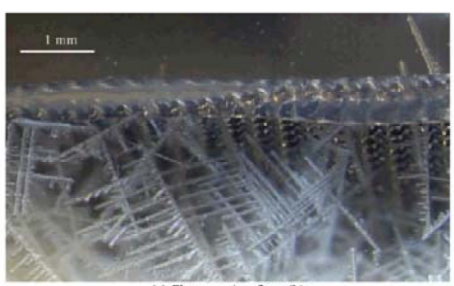
Hydrate formation occur not only on the interface but also in bulk water



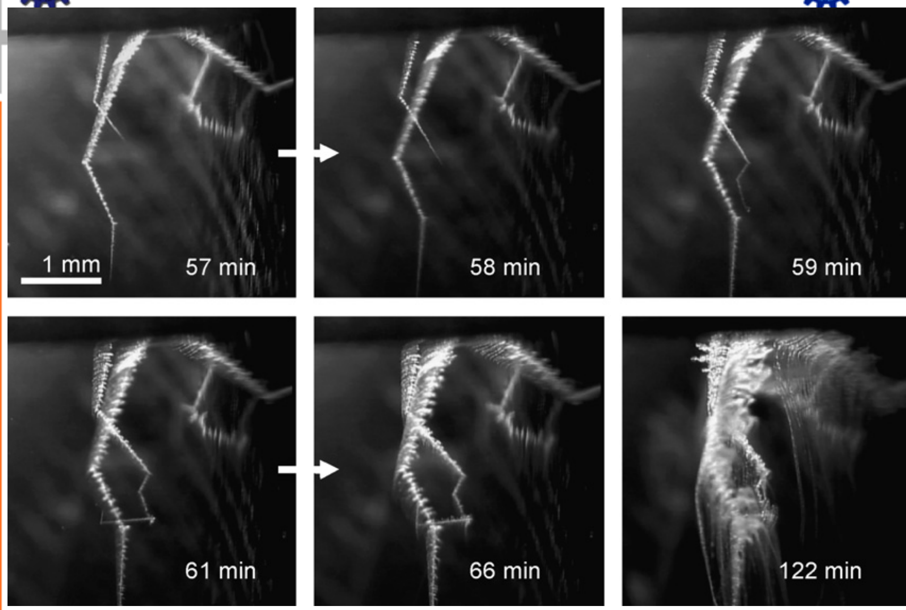
(a) Beginning of experiment

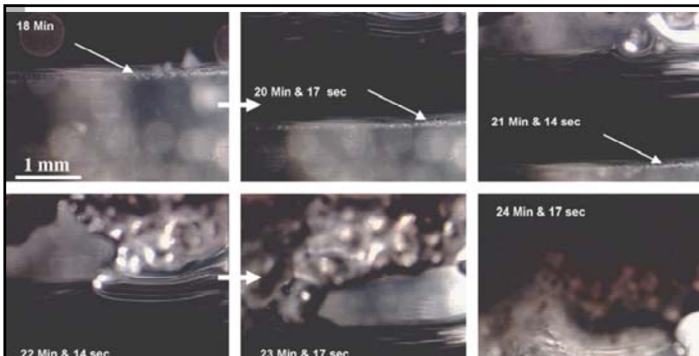
(b) after 41hr



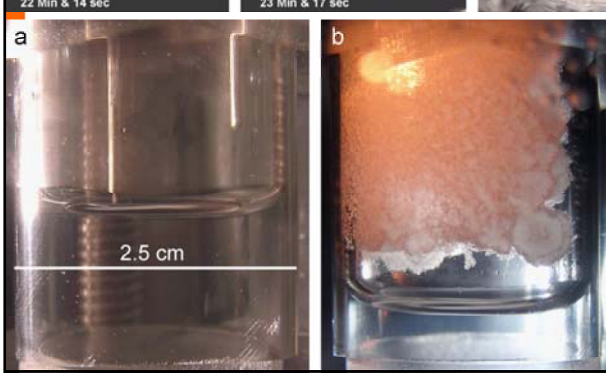
(c) Close-up view from (b)

Hydrates formed in presence of small percent of surface modifier (in this case an hydrate inhibitor) shows zig-zag growth pattern …





There is no link between the hydrate layer and The aqueous water layer underneath

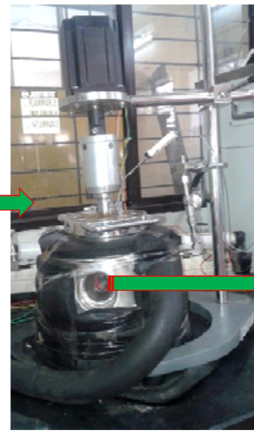


Hydrates in presence of higher concentration of kinetic inhibitor does not nucleates on the water – gas interface rather it nucleates some where in the gas phase with a very strange phenomena (Bridge effect?)

Lab scale setup to experimentally identify the additives

Hydrate Formation conditions:
Gas used: Pure CH_4; Pressure: 5.0 MPa; Temperature: 274.15 K

Stirred Tank Reactor with optical window



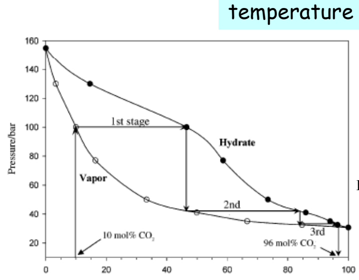
Hydrate Based Gas Separation (HBGS) Process for separating a gas mixture

Feed gas (CO_2/ H_2)
+
Water

Hydrate crystallization under suitable temperature and pressure

CO_2 depleted gas phase

CO_2 enriched hydrate phase



Kang, S.-P., and H. Lee, *Environ. Sci. Technol.*, 34, 4397-4400 (2000)

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Path to commercialization

HBGS Process

Static Mixer
- Energy Intensive
- Hydrate plug
- Large Volumes

Stirred Reactor
- Intrinsic Kinetics
- P & T measurements
- Laboratory scale

Fixed Bed
- Large contact area
- No stirring costs

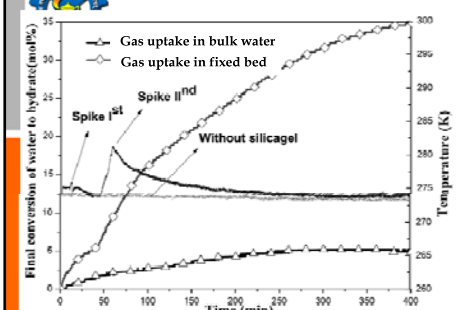
Unstirred Reactor
- Immiscible additive
- No stirring costs

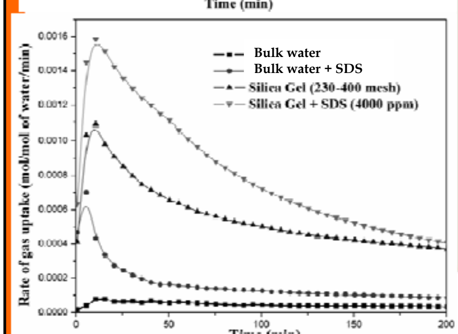
Energy Intensive; not suitable for large volumes
Solid hydrate formation in static mixer
Good for P & T measurement
Good for additives selection

Commercialization Potential Exists!

Two major challenges

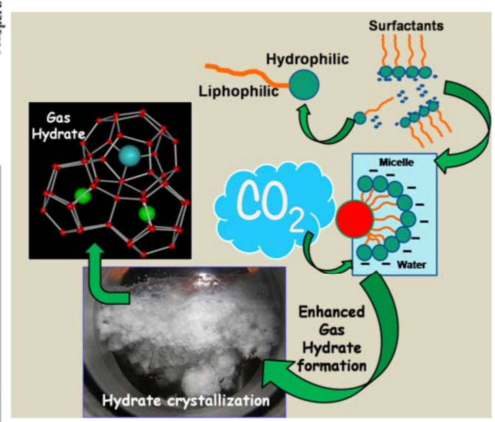
1. Improvement in kinetics of hydrate formation and water to hydrate conversion
2. Effect of impurities like fly-ash, SO_2, H_2S on separation efficiency





Influence of additives on hydrate formation kinetics

Kumar A, Sakpal T, Linga P , Kumar R.
Fuel., 105, 664 - 671 (2013).



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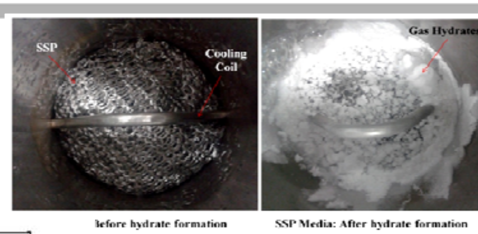

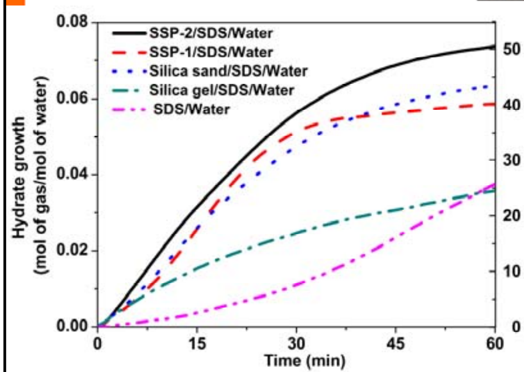

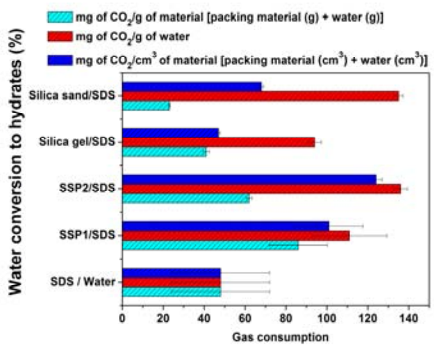

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Thank you !
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