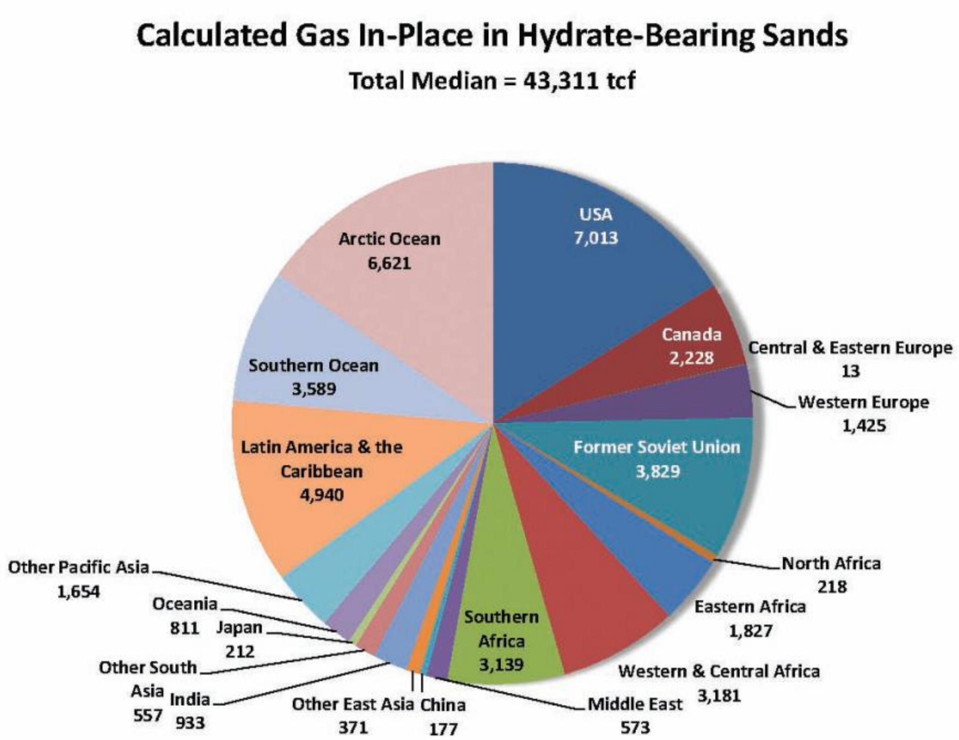
Combined CO2 storage in hydrate with simultaneous release of CH4 and limitations of adding N2 to the CO2

*

*2nd World Congress on Petroleum and Refinery



Source:

Arthur H. Johnson,

Hydrate Energy International

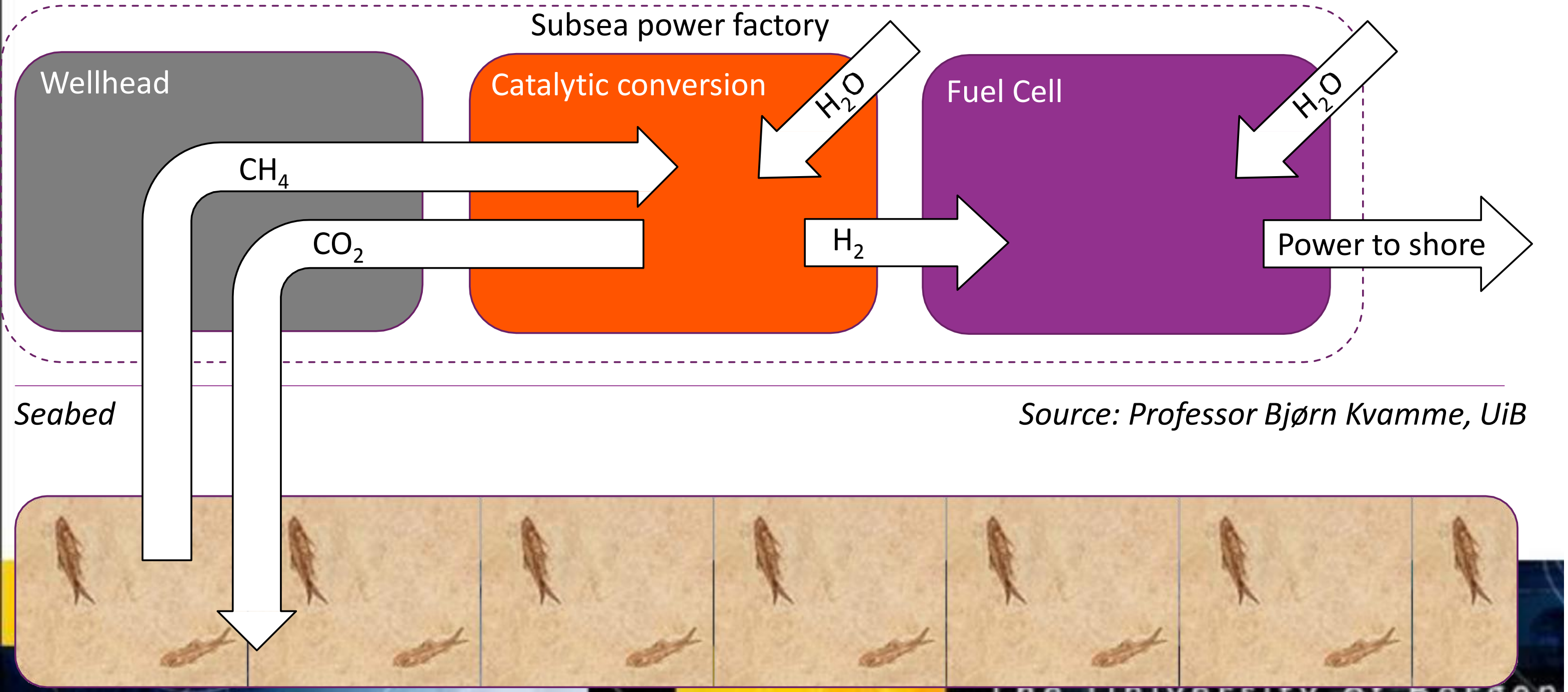
Bjørn Kvamme*
University of Bergen

Contact: Professor Bjørn Kvamme
Department of Physics and Technology, University of Bergen, Bergen, Norway
Bjorn.kvamme@ift.uib.no

MOTIVATION

Combined ***storage of CO_2*** and ***release of in situ CH_4*** from hydrate is feasible, as demonstrated through years of theoretical investigations, experiments and a pilot plant. ***Steam conversion of CH_4 to H_2*** and CO_2 is even available on a ship installation, and can be made sub-sea. Transport of H_2 to shore or sub-sea power generation are options

Zero emission energy generation system



Source: Professor Bjørn Kvamme, UiB

The concept is from an application to FRINATEK by Bjørn Kvamme Spring 2016 **"From hydrocarbon age towards hydrogen age".** Thanks to Bjarte Langeland, Stinger, for the illustration

Clean energy

- The H2IC0.2 FPSO is an all-new facility developed to carry out steam reforming of APG generated by offshore plants above subsea oil fields, convert it to CO_2 and hydrogen, and extract the resulting CO_2 and hydrogen. Can it be made on a rocking ship it can be made into sub-sea.

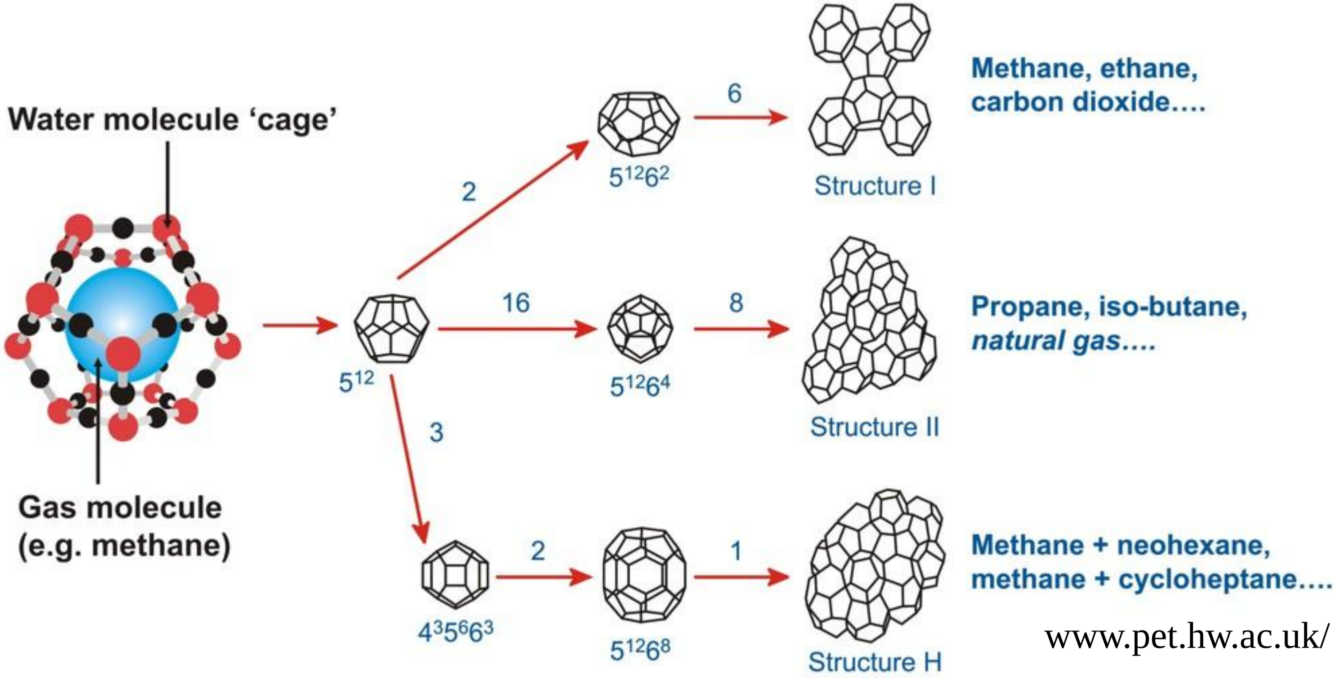
- Transport of hydrogen to shore or sub-sea convertion to energy (fuel cells) is clearly realistic

Toyota Mirai is not the first hydrogen car in Norway but the promise of 20 new filling stations in 2017 is a positive signal

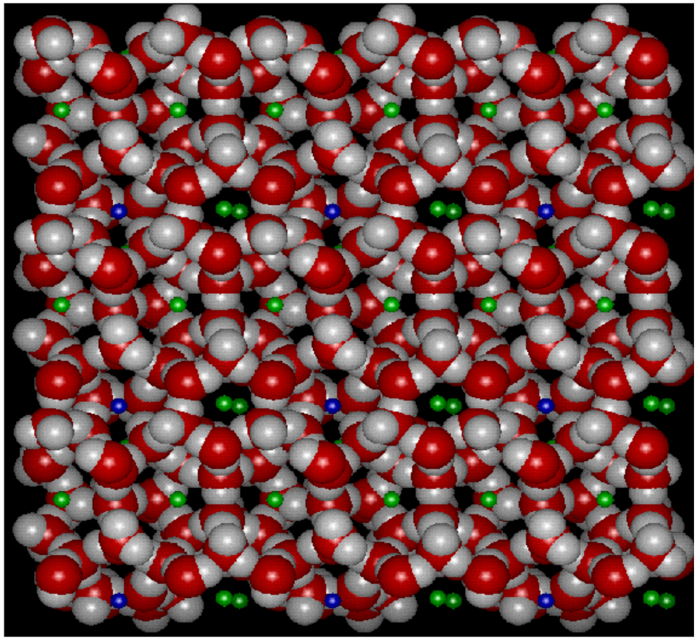
The ship contains complete separation facility and also toluene hydrogenation reaction applying the "organic chemicalhydride (OCH) method", becoming fixated as methylcyclohexane (MCH) which can be stored in liquid form at ambient temperature and pressure.

OUTLINE

- Ignik Sikumo – a pilot plant study on injection of CO_2/N_2 into CH_4 hydrate
- Mechanisms for conversion of CH_4 hydrate over to CO_2 dominated hydrate with associated methane release
- Non-equilibrium nature of hydrates in porous media
- RCB – the first non-equilibrium hydrate simulator



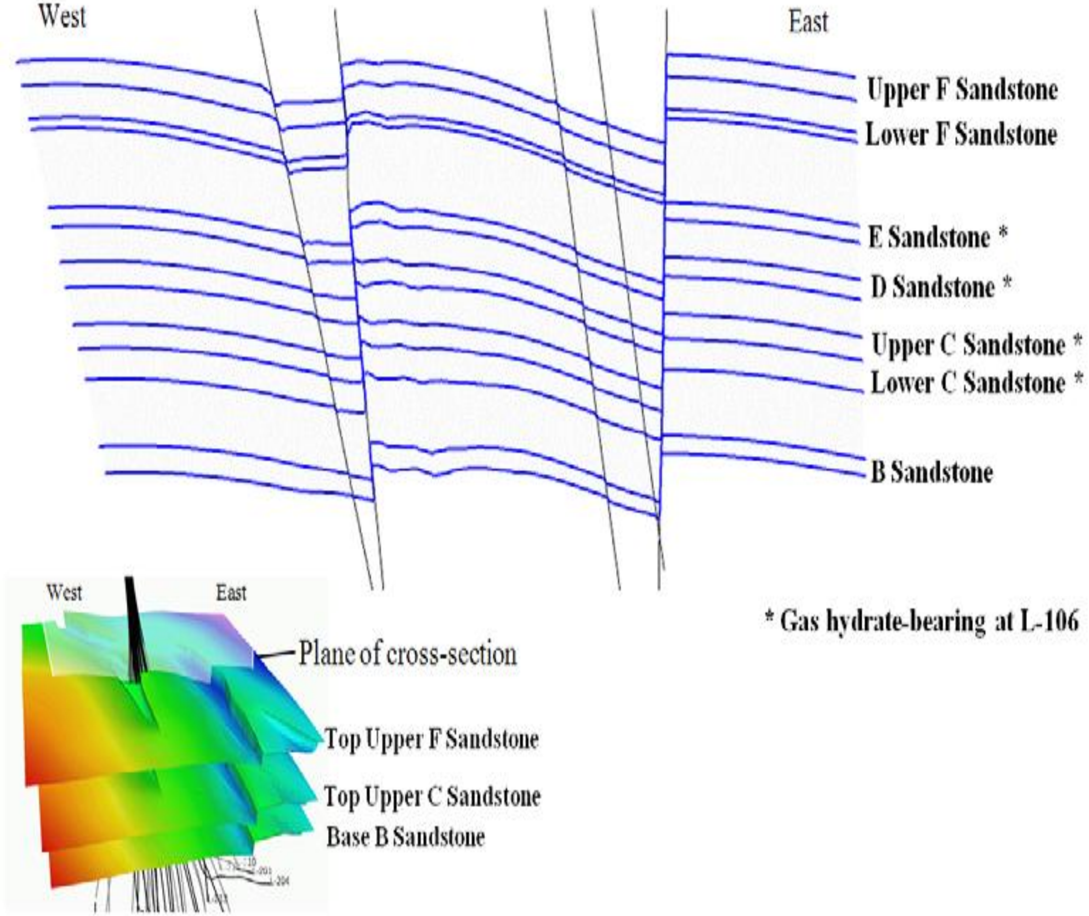
www.pet.hw.ac.uk/



Red is oxygen and grey is hydrogen in water. Ethane in large cavities (green) and methane in small cavities (blue) of structure I is scaled down.
Volume of water in hydrate is roughly 10% larger than in liquid water.

Department of Energy, ConocoPhillips and JOGMEC, Japan were interested enough to put money on the table

The Ignik Sikumo field test was conducted by Conocophillips and JOGMEC



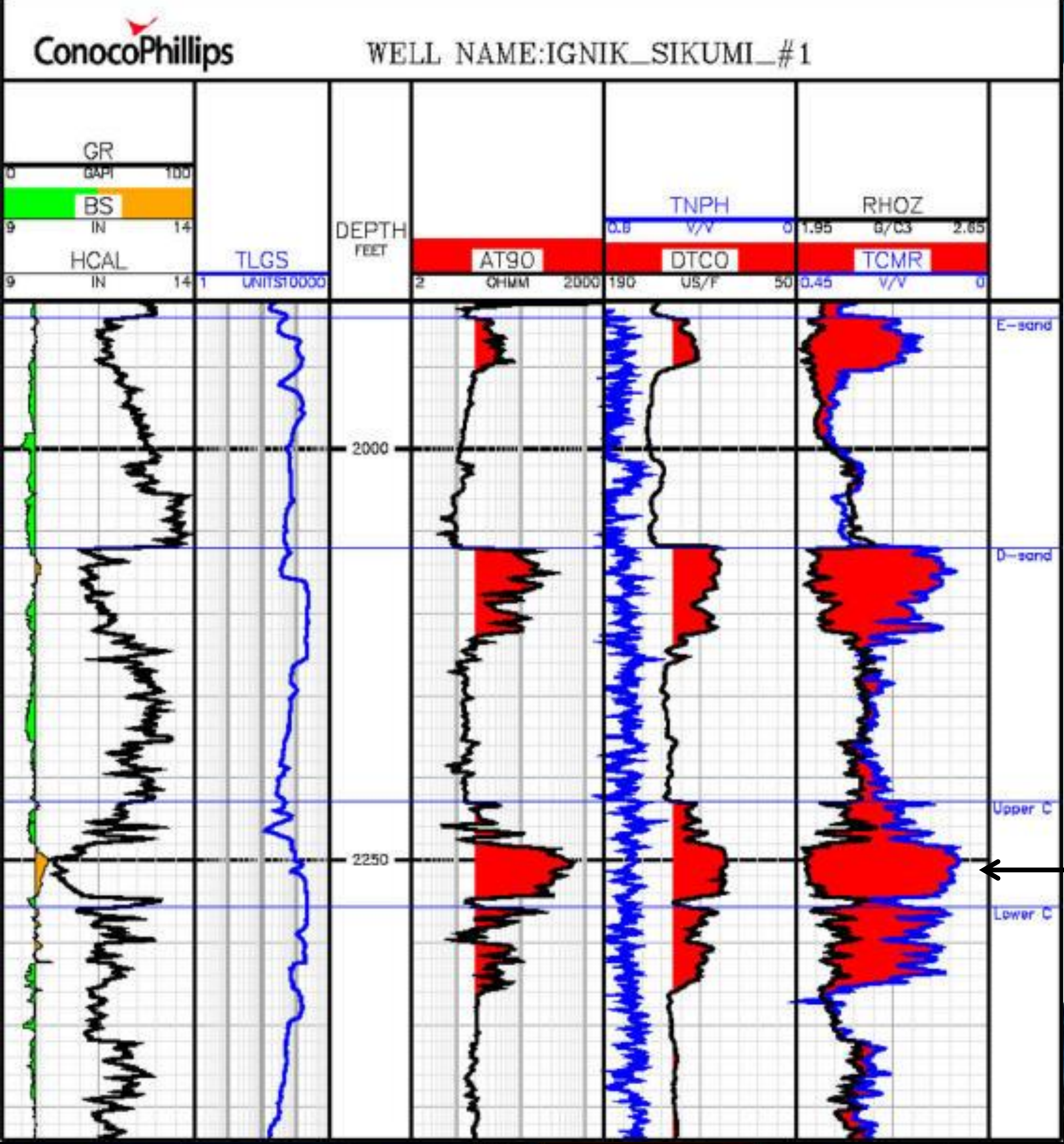
* Gas hydrate-bearing at L-106

While different laboratories around the world has investigated the CO_2/CH_4 exchange for the last 2 decades only one pilot plant study has been conducted.

Estimated hydrate saturation in the socalled upper C was 75 %, 15 % free water and rest pore bounded water

What do we actually know about the conversion mechanisms ?

Various methods to identify hydrate saturation



For details on figure: Kvamme, B., Thermodynamic limitations of the CO_2/N_2 mixture injected into CH_4 hydrate in the Ignik Sikumi field trial, 2016, J. Chem. Eng. Data, 2016, 61 (3), pp 1280–1295

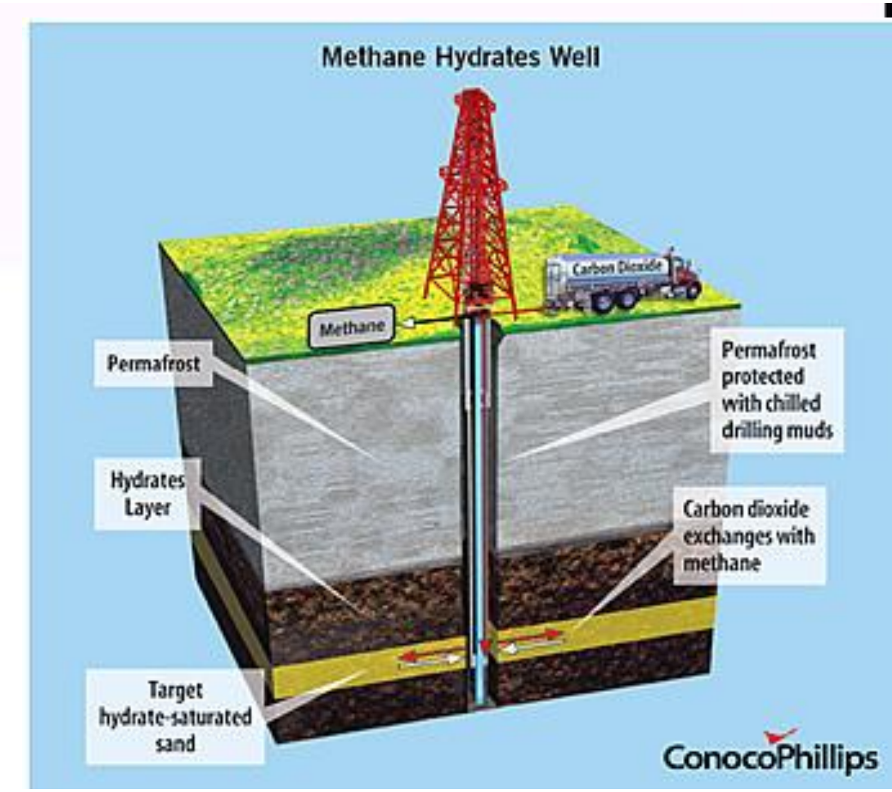
Target section for test production

The pilot plant in Alaska was conducted using only one well in an «huff and puff» method

- This implies that a period of injection is followed by a reduced pressure production period.
- Due to the high density of CO_2 the neccesary injection pressure would be too high for pure CO_2 to enter the formation without geomechanical implications
- A mixture of 22.5% CO_2 by volume and 77.5% N_2 was injected. Some nitrogen will enter small cavities of the final hydrate. Rates and timeline in next slide.
- This mixture will have sufficient relative permeability but nitrogen dilutes the CO_2 and reduces thermodynamic driving force for conversion
- Active section stimulated: A layer between 700 and 800 m below ground

Ignik Sikumo

The first large scale pilot test of CO_2 based CH_4 hydrate production was completed April 10, 2012

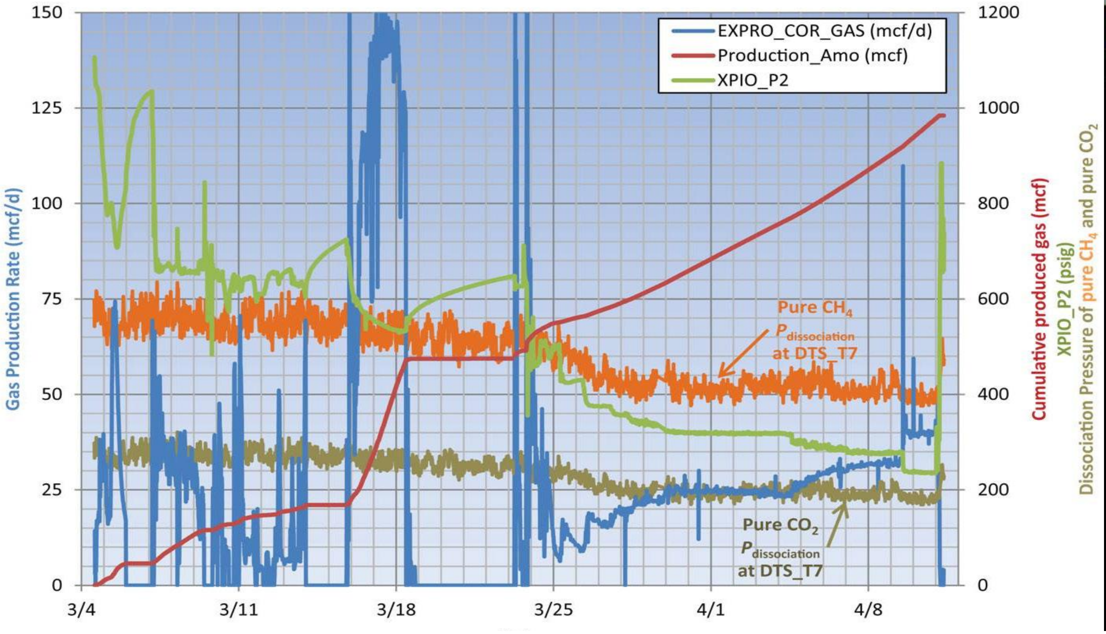


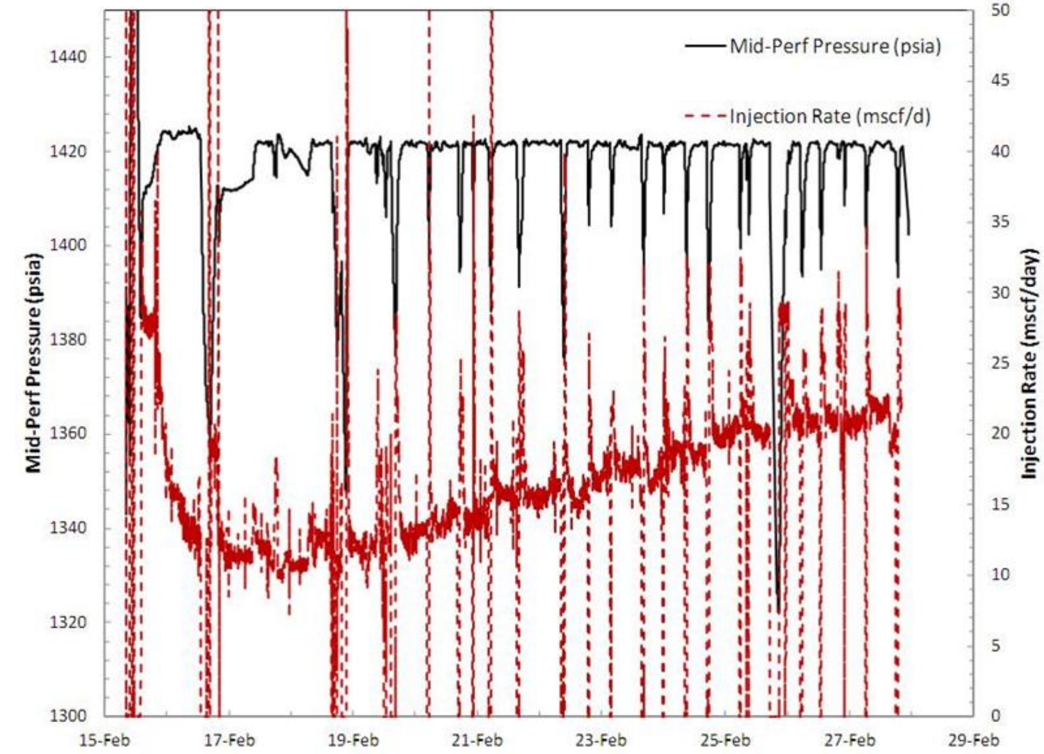
The complete report is open and can be downloaded from DOE web-pages for the hydrate program

These snapshots can also be found in the report summary as presented in short form in the «Fire in the ice» March 2013 issue

Right: production (red) from March 4 to April 9

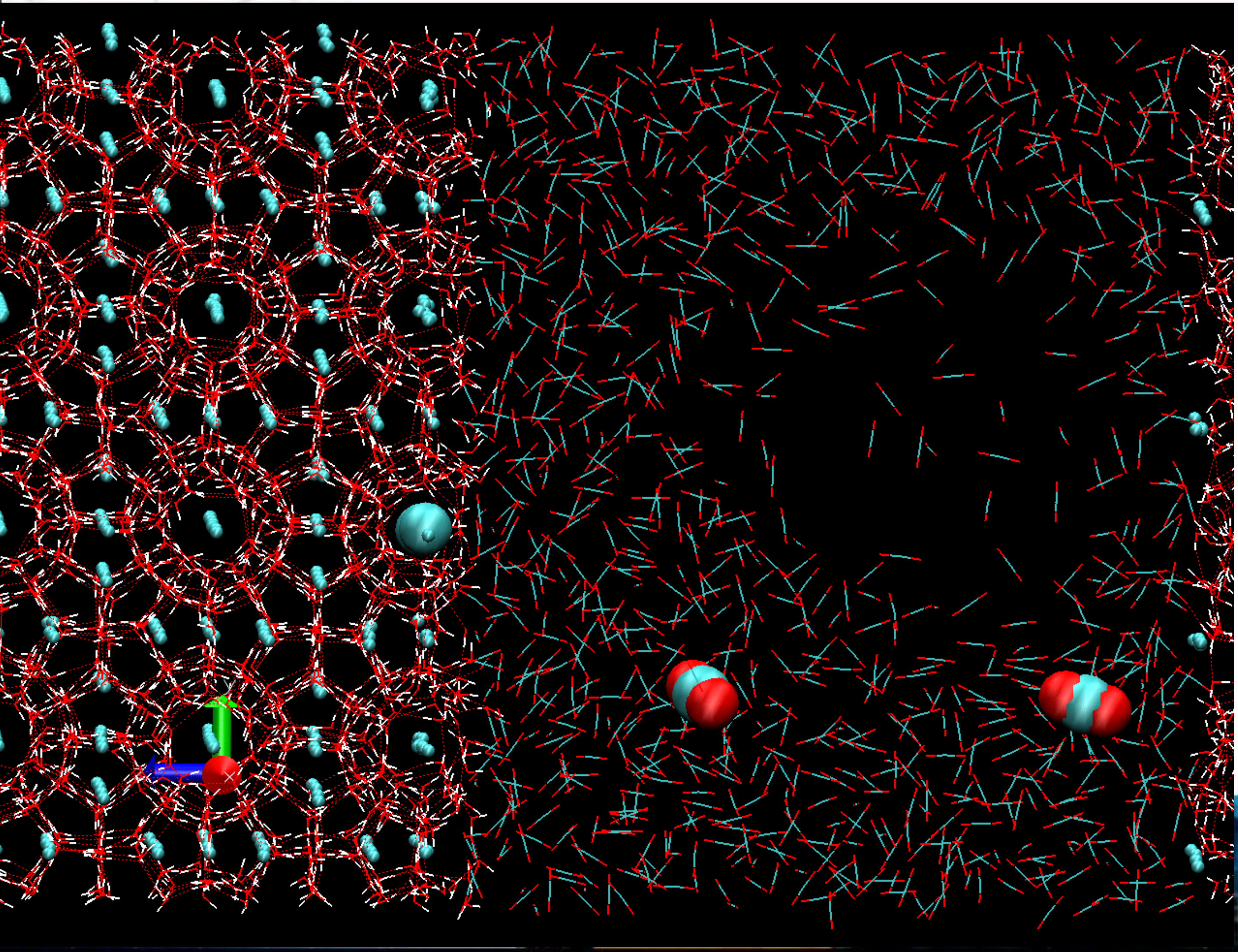
Below: injection rate (red) for 2 weeks injection (Feb 15 to Feb 29)





A problem with the «huff and puff» for injection of CO_2/N_2 mix is that the released CH_4 will reduce the trapped gas density. In a continuous production in a two well completion this would give a perfect drive from injection well towards production well(s) and reduce associated water and sand production compared to the one well solution, in which the reduced fluid density would enhance a draw of water as well as sand when pressure was reduced again.

Conversion mechanisms:
1. Solid state conversion



Solid state conversion is slow, with diffusivity coefficient in the order of 10^-16 m^2/s

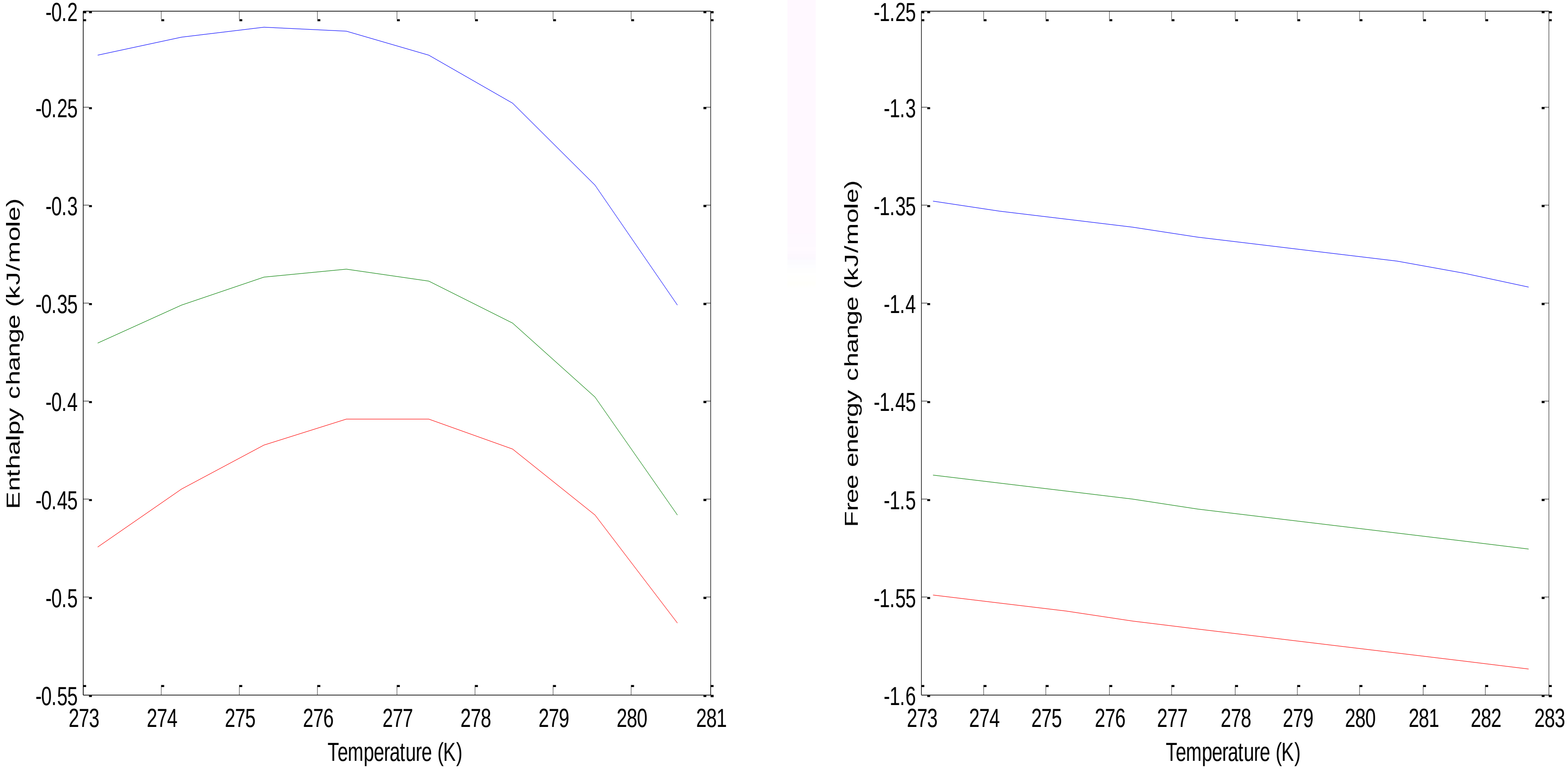
The process in entropy dominated (see next slide)

This mechanism has been verified experimentally by Ripmeester et.al.

The relative impact of this mechanism will increase with lower free water in pores

Free energy and enthalpy changes for conversion from pure methane hydrate to pure carbon dioxide hydrate

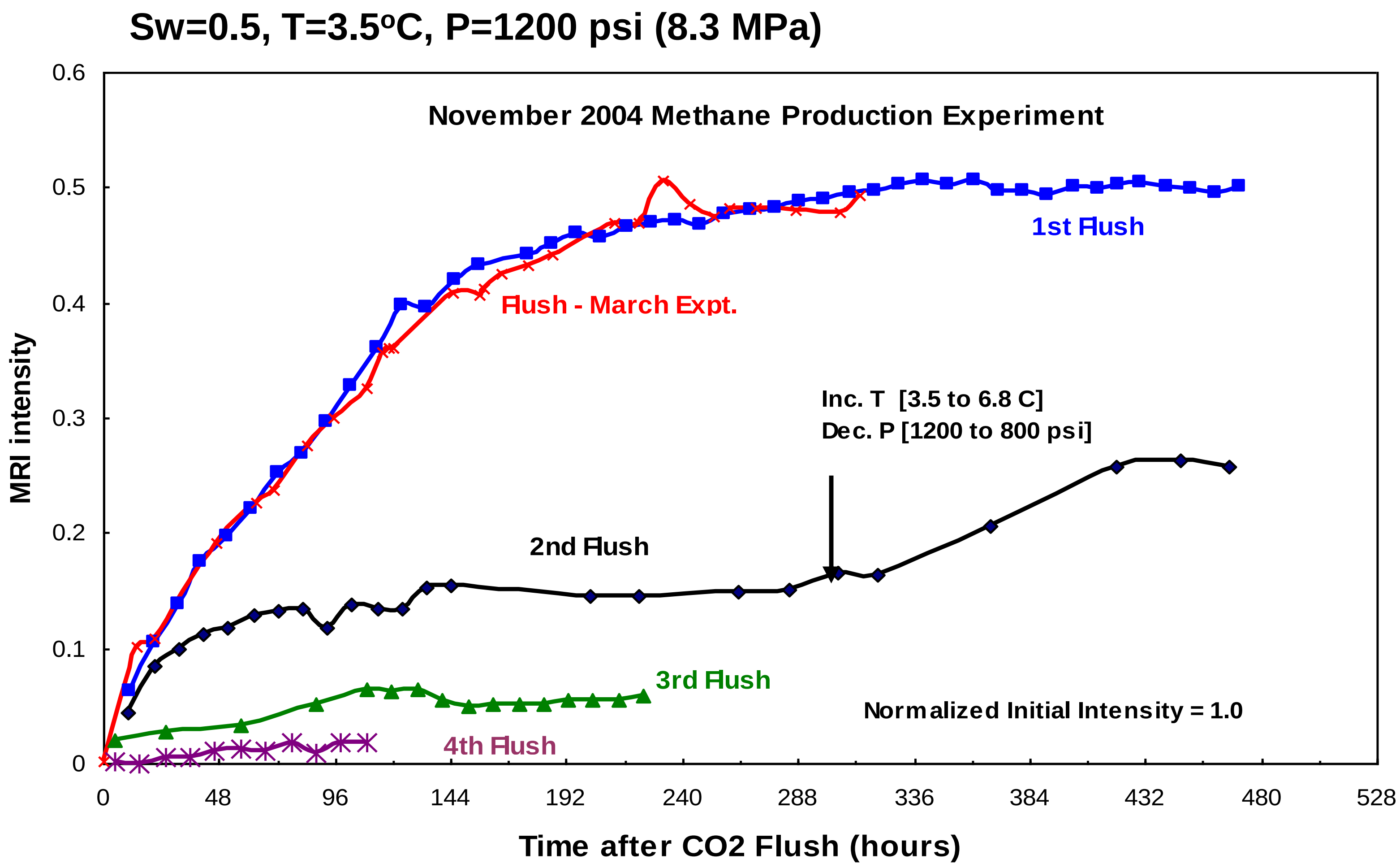
Blue: 43 bar, **Green: 83 bar**, **Red: 120 bar**



Free energy chage for the water in the structure is not large. CO_2 change is also limited since it comes from a fairly dense phase and have reasonable filling. But CH_4 will benefit from the entropy change of getting released.

CH_4 Production Rates & Amounts from Hydrate

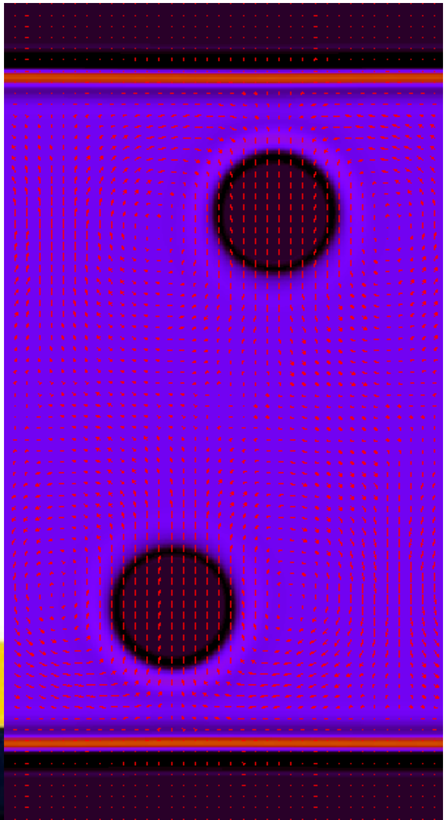
MRI intensity almost directly translated to fraction converted



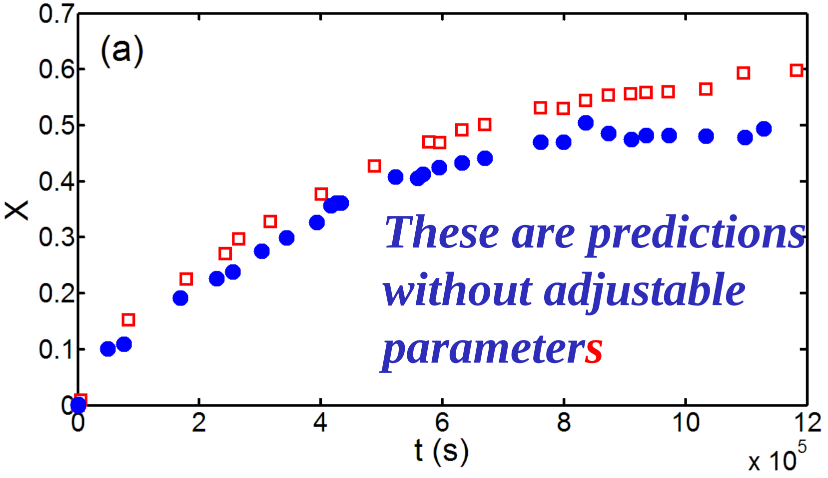
- *So what is the thermodynamics involved in this transformation and what is the conversion mechanism?*

So what makes the exchange of CH_4 hydrate over to CO_2/CH_4 mixed hydrate possible?

- ***Molecular modeling can verifiy the solid state exchange mechanism experimentally detected by several reserach groups but maybe most detailed by Ripmeester et.al. But the process is very slow – with diffusivities in the order of 10^-16 square meter per second***



Phase Field Theory predictions of CO_2 conversion of CH_4 (blue) hydrate X(t) versus experiments (red)



These are predictions without adjustable parameters

- *Phase Field Theory modelling of the experiments for exchange between CO_2 and CH_4 indicates an average diffusivity of 10^-12 square meter persecond and obviously composite mechanisms. A closer look at the systems with present generation of our PFT theory gives deper insight*

2- Second mechanism

- New CO_2 hydrate forms from injected CO_2 and free water in the pore volume.
- Heat released will contribute to dissociation of *in situ* CH_4 hydrate.
- This also explains why some of the injected N_2 was trapped in the CO_2 hydrate since N_2 may assist in stabilization of the hydrate by filling small cavities.

Three component Phase Field Theory with implicit hydrodynamics

$$\mathrm{F} = \int d\underline{r}\left(\frac{\varepsilon_{\phi}^{2}}{2}T(\nabla\phi)^{2} + \sum_{i,j=1}^{3}\frac{\varepsilon_{xi,j}^{2}}{4}T\rho\left(x_i\nabla x_j - x_j\nabla x_i\right)^{2} + f_{bulk}(\phi, x_1, x_2, x_3, T)\right)$$

$$f_{bulk} = WTg(\phi) + \left(1 - p(\phi)\right)f_S(x_1, x_2, x_3, T) + p(\phi)f_L(x_1, x_2, x_3, T)$$

$$f_S = G_S\rho_m^{hyd}, \qquad f_L = G_L\rho_m^{L}$$

$$\frac{\partial\phi}{\partial t} + (\vec{v}.\nabla)\phi = -M_{\phi}(\phi, x_1, x_2, x_3)\frac{\delta F}{\delta\phi}$$

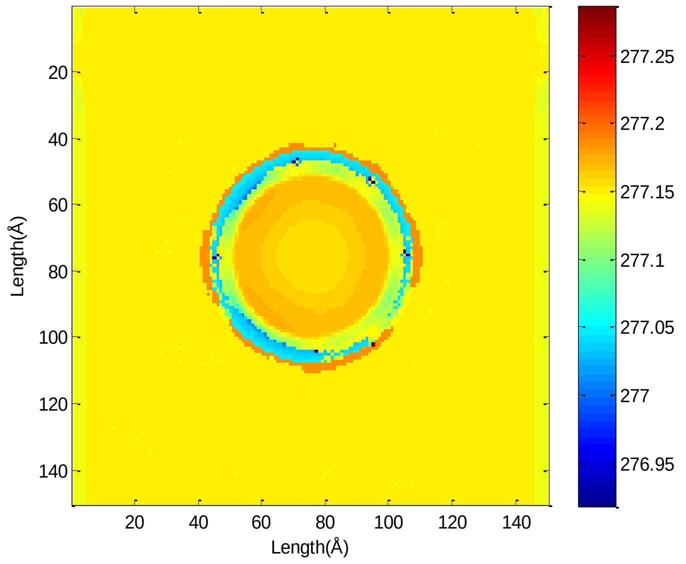
$$\frac{\partial x_i}{\partial t} + (\vec{v}.\nabla)x_i = \nabla.\left(M_{xi}(\phi, x_1, x_2, x_3)\nabla\frac{\delta F}{\delta xi}\right)$$

$$\frac{\partial\rho}{\partial t} = -\rho_m\nabla.\vec{v}$$

$$\rho\frac{\partial\vec{v}}{\partial t} + \rho(\vec{v}.\nabla)\vec{v} = \rho\vec{g} + \nabla.P$$

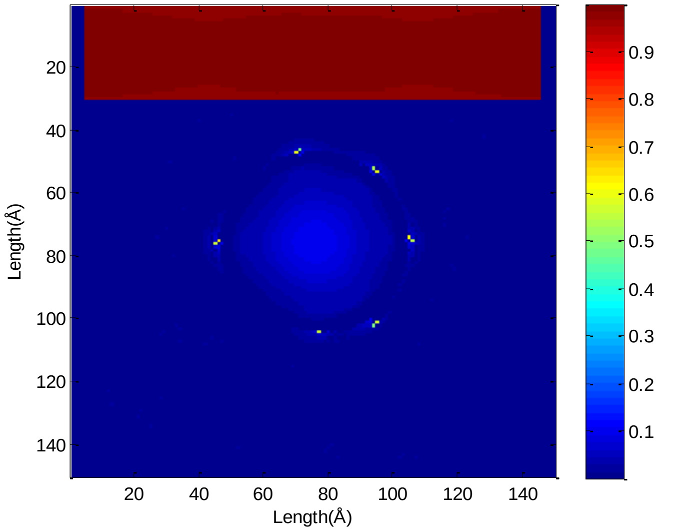
$$P = \xi + \Pi$$

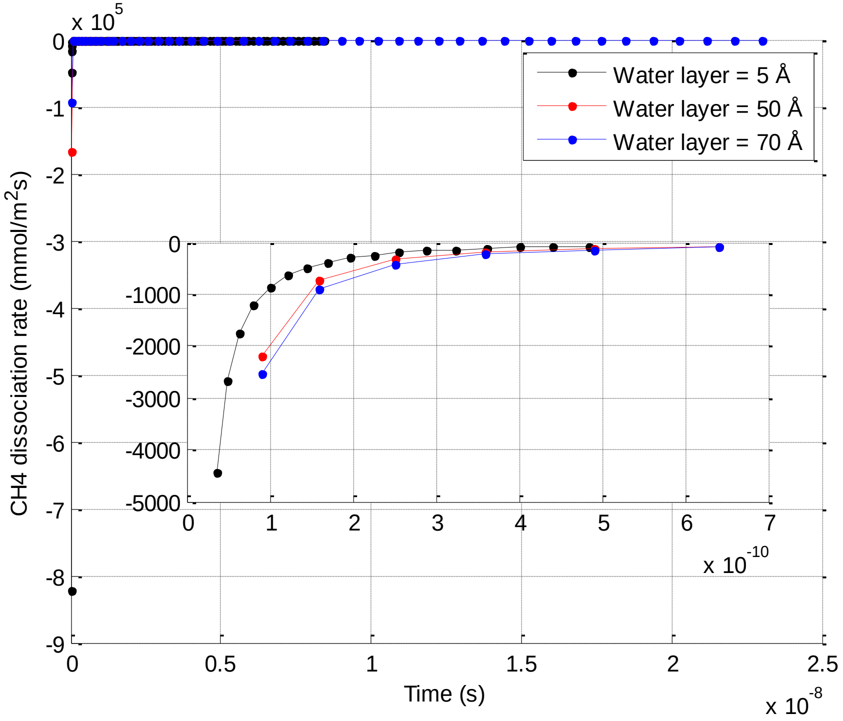
Parameters ε and w can be fixed from the interface thickness and interface free energy. ε ij set equal to ε



It may not be easy to read from these figures but heat released from new CO_2 hydrate formation mainly goes inwards through liquid water and hydrate while local cooling during in situ CH_4 hydrate is smeared more out on interface towards CO_2 due to low heat transport capacity of CO_2.

The thicker initial liquid water film around hydrate the longer period of fast exchange. I.e.: Free pore water is the key

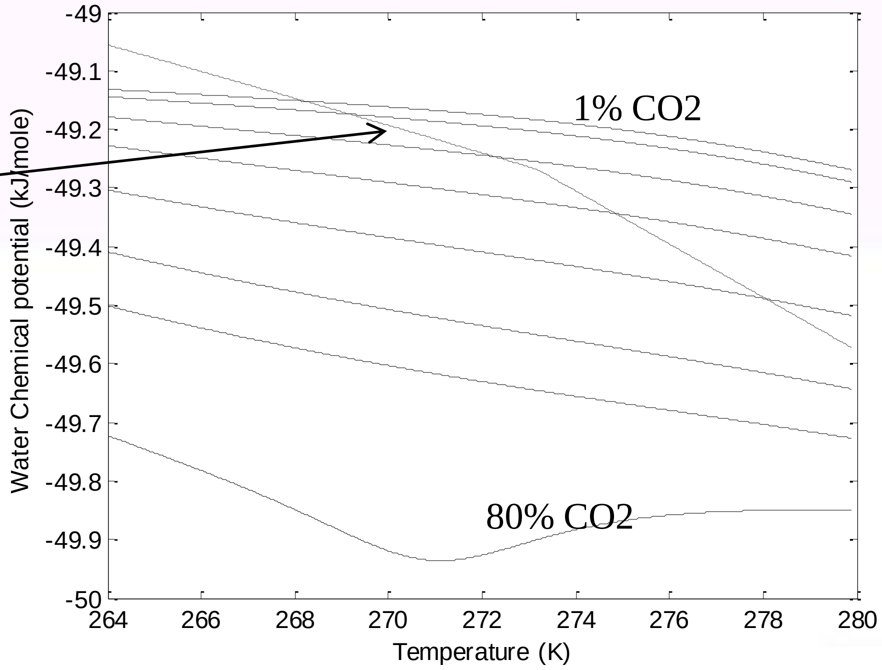




Adding large amounts of N_2 has several drawbacks and is not the right direction forward on combined CO_2 storage and clean energy production.

Formation of new CO_2 dominated hydrate is only possible if hydrate water chem.pot. (solid) is lower than liquid water chem.pot. (dash)

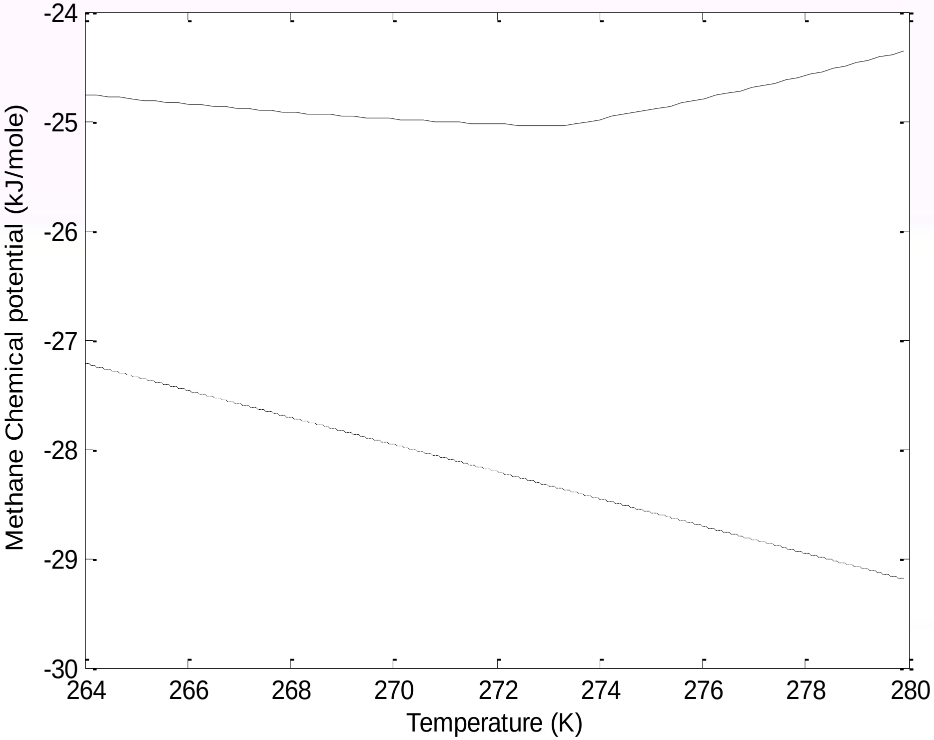
- CO_2 ***dissolves*** in water,
- CO_2 ***adsorbs*** on mineral surfaces
- Creation of ***new hydrate*** will extract ***CO_2*** from the mixture
- There must be a ***lower limit for CO_2*** in the gas for creation of new hydrate and feasibility ***for the fast mechanism***



- **Estimated water chemical potential in hydrate (solid) and liquid water (dash) as function of temperature for 80 bars and CO_2 mole-fractions of 0.80, 0.6, 0.4, 0.2, 0.1, 0.05, 0.02, 0.01, with 0.80 mole-fraction curve lowest and 0.01 mole-fraction curve on top.**

But CH_4 hydrate will still dissociate towards N_2 which is undersaturated on CH_4

- But the kinetic rates are low !
- Hydrate will also dissociate towards water undersaturated with methane so during flow and fluid exchange in the pores many different scenarios are possible



Estimated chemical potential for CH_4 in equilibrium hydrate (-) versus chemical potential for 10 mole % CH_4 mixed into a gas phase originally containing 1mole % CO_2 and rest N_2 (--) at 80 bars pressure. Pressures on the solid curve are the estimated equilibrium pressures for pure CH_4 hydrate

Adding small amounts of N_2 (max roughly 25%) is good but then other additives in addition to N_2 is the key

Kvamme, B., UoB: US Patent 8129316 : Method of creating a carbon dioxide hydrate

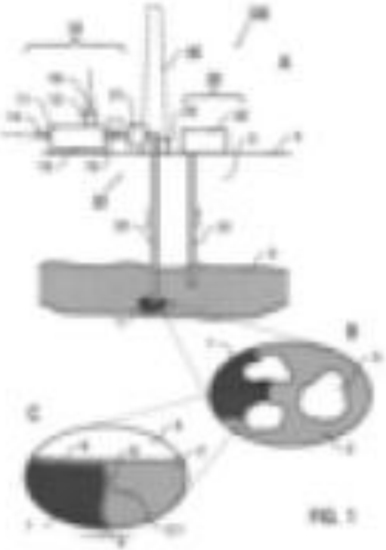


FIG. 1

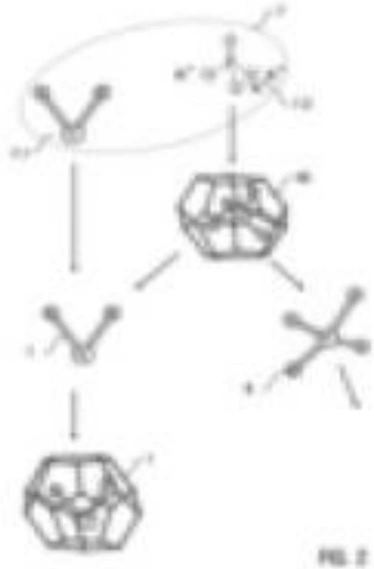


FIG. 2

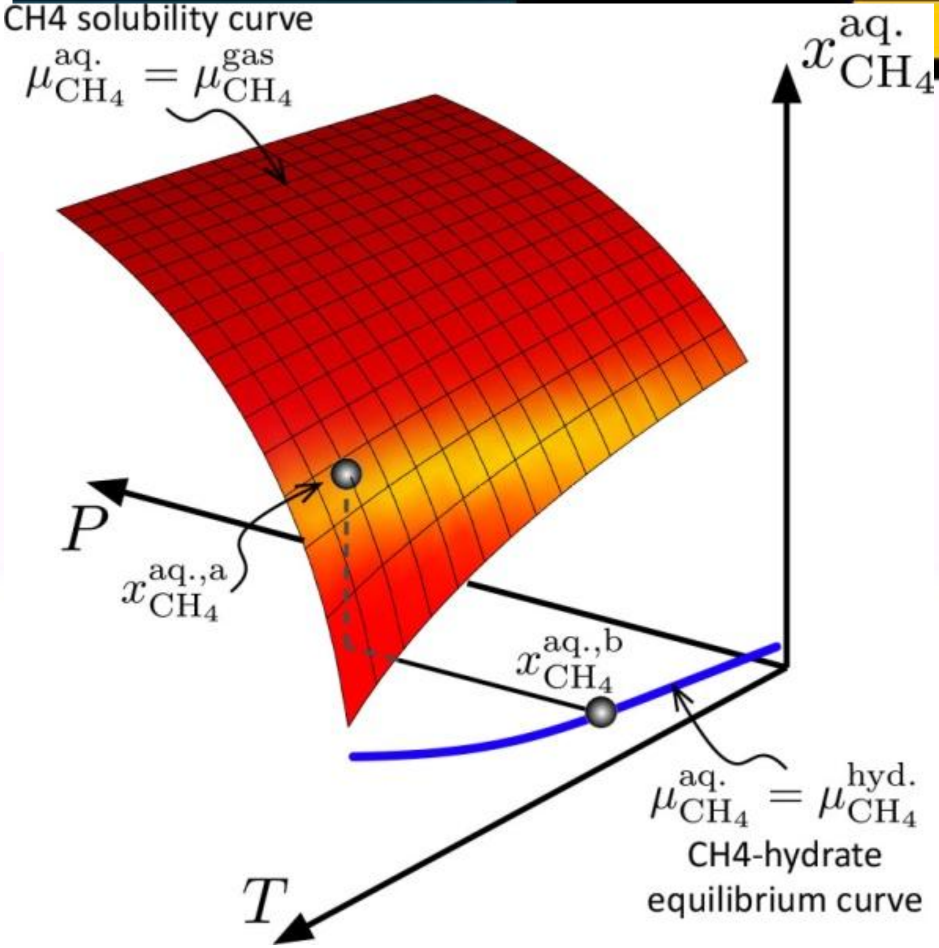
- Adding surfactants to the CO_2 serves 2 purposes:

1) Dissociating in situ hydrate
2) Reduce blocking of pores due to new CO_2 hydrate

Yet another patent idea is on it’s way to being fomalized. This new concept consist of no harmful components/chemicals. The above patent involves a variety of choices of chemicals, of which many are environmentally friendly.

RCB – a new hydrate reservoir simulator

- Hydrates in porous media cannot reach thermodynamic equilibrium and depends on sealing mechanisms (clay, shale)
- There is a need for a hydrate reservoir simulator which can take into account competing phase transitions of formation and dissociation under constraints of mass and heat transport



Hydrate can form from ***dissolved CH4*** in water if concentration is ***above blue curve***. Red contour is CH4 solubility in liquid water. Hydrate dissociates in CH4 concentration in water is ***below blue curve***

Khadijeh Qorbani, Bjørn Kvamme, Using a Reactive Transport Simulator to Simulate CH4 Production from Bear Island Basin in the Barents Sea Utilizing the Depressurization Method, Energies 2017, 10, 187

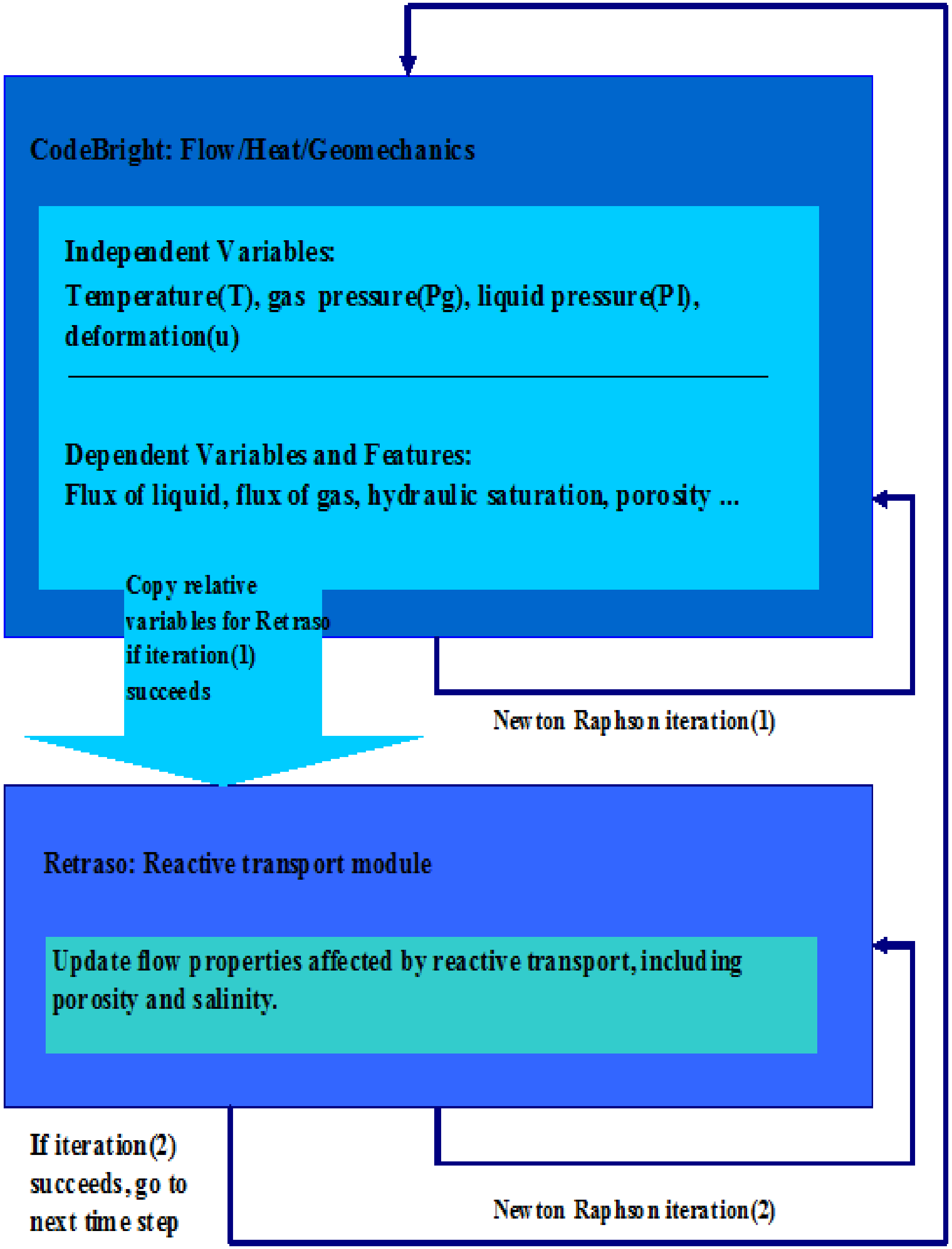
RetrasoCodeBright is *the only CO_2 storage simulator* with *appropriate handling of hydrate*

- ***State of the art reactive transport modules*** (similar to EQ3/6 and with options for PHREEQ and other data bases)

- Adequate description of ***fractures as hydrodynamic channels*** (not funded yet)

- ***Several geomechanical models*** built in and easy incorporation of alternative models

- ***Userfriendly graphical interface*** for easy setup of new systems and presentation of output (files, figures, animations)



CodeBright: Flow/Heat/Geomechanics

Independent Variables:
Temperature(T), gas pressure(Pg), liquid pressure(Pl), deformation(u)

Dependent Variables and Features:
Flux of liquid, flux of gas, hydraulic saturation, porosity ...

Copy relative variables for Retraso if iteration(1) succeds

Newton Raphson iteration(1)

Retraso: Reactive transport module

Update flow properties affected by reactive transport, including porosity and salinity.

If iteration(2) succeeds, go to next time step

Newton Raphson iteration(2)

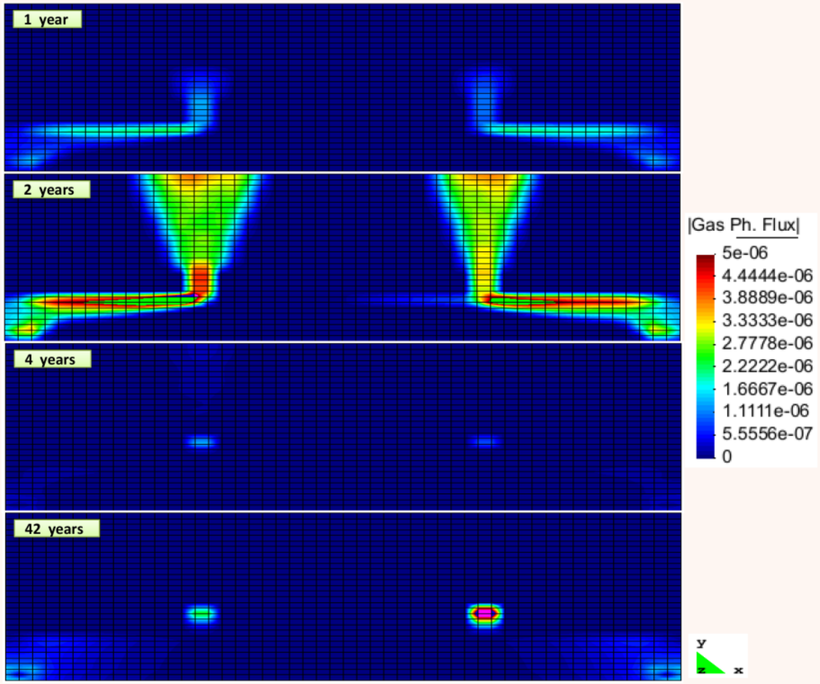
Fig 1 RCB solves the integrated equations sequentially in one time step.

Hydrate formation is a possible effect in aquifer reservoirs which can be candidates for CO_2 storage

- Impact of ***hydrate formation during aquifer storage of CO_2*** has been a dedicated effort in FME-SUCCESS

- This has also been ***a general discussion in the CO_2 aquifer storage community***, including publications from Kvamme's group

- And regardless of how deep the CO_2 injection is (except extreme conditions where density of CO_2 is higher than groundwater density) the ***CO_2 plume may enter hydrate formation regions.***



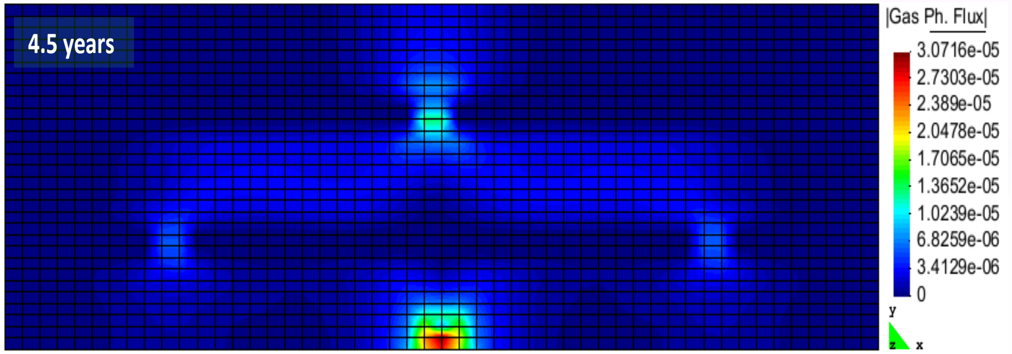
Simulation of CO_2 injection in a system with two small fractures and hydrate forming conditions above the fractures. After one year (top) flow through fractures is slow. After two years hydrate is growing but still not blocking (next) while after 4 years CO_2 flux is reduced to a low value (3rd) and after 42 years (bottom) the system is very stational with very low CO_2 flux.. Without hydrate formation situation is similar to fig2 also after 42 years.

The fast mechanism for conversion of CH_4 hydrate involves formation of new CO_2 dominated hydrate from the free pore water. If formation is substantially faster than dissociation we expect reduction in available pore volume locally

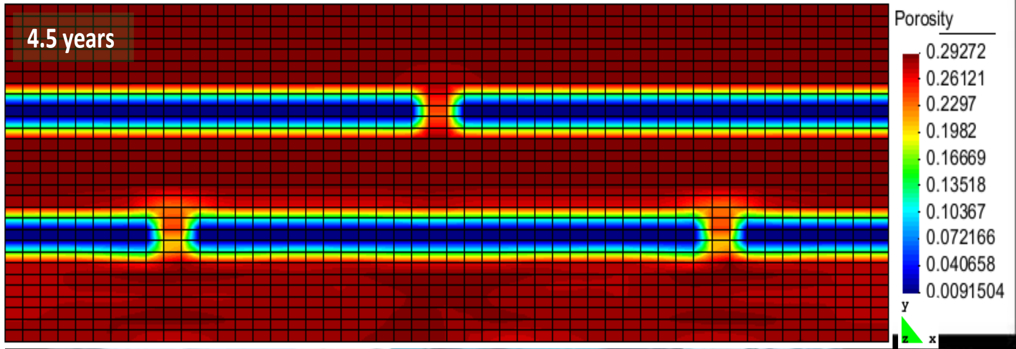
- The formation of a new ***CO_2 hydrate is the primary mechanism*** in Kvammes US patent, as well as the new patent and as such this part is not special.

- The released heat from CO_2 hydrate formation assist ***in dissociating CH_4 hydrate*** and releasing CH_4 gas for energy if the CO_2 is injected in the CH_4 hydrate formation or close enough.

- If ***injected*** in aquifer ***below CH_4 hydrate*** a formed CO_2 hydrate will establish below CH_4 hydrate ***and provide extra CO_2 storage sealing.***



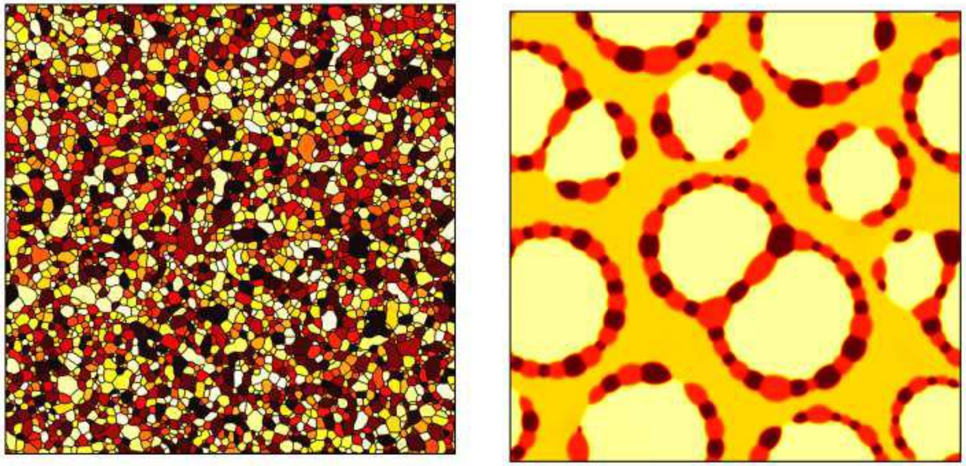
CO_2 flux (above) 4.5 years of injection and changes in apparent porosity (below) as avaliable pore volume fractions for fluid filling.



Japan is even going to do a long term test (minimum 6 months)

Although the initial test will start with pressure reduction the ***use of CO_2 is high on the research agenda for longer terms*** (also keep in mind that JOGMEC was a substantial economic supporter to the Ignik Simumi CO_2/N_2 test)

- Sub-sea steam ***cracking of conventional hydrocarbons*** are also a possible spinoff in long terms
- Supply of CO_2 to other types of ***utilization like EOR*** is also a possible spinoff.



Multiscale modeling of progress of water/CO2/emulsifier/hydrocarbon emulsions helps in understanding new emulsifiers

Japan is not the only country with hydrate energy high on the agenda

- India
- New Zealand
- Korea
- Taiwan
- China

and several other countries have ***substantial** hydrate resources* and ***limited** conventional sources of fossil fuel*

Norway is in the front seat of key technology like:

- Design and operation of sub-seainstallations
- Drilling – including new concepts for slim-hole drilling (many slim wells are better than few ordinary wells)
- Offshore operations

Norwegian industry already deliveres equipment the Japan pilot test but ***Norwegian industry potential*** is huge

Conclusions

- Relevant aquifer reservoirs for CO_2 storage can contain ***hydrate formation zones which a CO_2 plume might reach***. Formation of CO_2 hydrate in those zones will provide extra storage sealing but also reduce vertical spreading in those regions.

- Storing CO_2 in reservoirs which already contains ***CH_4 hydrate*** can be an opportunity for ***simultaneous safe long terms CO_2 storage and revenues from clean (hydrogen) energy*** production that can pay for the costs of storage.

- Injection of CO_2 into reservoirs containing ***CH_4 hydrate*** but in aquifers below the CH_4 hydrate will just lead to an ***extra sealing*** hydrate layer ***below a sealed reservoir which have been proven as safe storage site for geological time scales***.

- Norwegian industry has unique well drilling expertise ***which can substantially reduce drilling costs*** for any type of aquifer storage of CO_2.

Acknowledgements

We genuinely appreciate financial support from STATOIL under contract 4502354080

1st ANNOUNCEMENT

FIERY ICE 2017 - *Corpus Christi, Texas, USA, 6-8 December 2017*

11TH INTERNATIONAL WORKSHOP ON METHANE HYDRATE RESEARCH AND DEVELOPMENT

Progress and Future International Directions

OVERVIEW: The 1st International Workshop on Methane Hydrate R&D was held in March 2001 in Honolulu, Hawaii. The primary objective of that and subsequent workshops was to provide a forum where hydrate researchers and stakeholders could freely exchange information and identify research priorities in an effort to promote collaboration. Subsequent workshops have been held, on average, every 1.5 years in different countries including the U.S., Chile, Canada, the U.K., Norway, New Zealand, Japan, and India. This effort has resulted in a broad range of field and laboratory research pertaining to gas hydrate distributions, stability and formation, and contribution to climate change and coastal ocean carbon cycling. Based on previous workshop focuses and developments in this field over the last 16 years, the 11th workshop will focus on;

1) Gas Hydrate Provision of National Energy; Exploration, Acquisition, and Economy;
2) Methane Contribution to Global Climate Change; Arctic, Antarctic and in between locations;
3) Natural and Anthropogenic Contributions to Coastal and Industrial Platform Stability; and
4) Carbon Dioxide Injection In Terms of Methane Acquisition and Environmental Safety.

We hope that previous participants in this workshop series, as well as other interested parties, will be able to join us in Corpus Christi this winter December 6th through 8th, 2017.

AGENDA: The 11th Workshop will follow the format that has successfully been employed in our previous meetings. The workshop will include plenary lectures, oral presentations and posters, and breakout sessions.

REGISTRATION AND ABSTRACTS: The Workshop website is under construction and is expected to be operational May 2017. The 2nd Announcement will be distributed electronically once the website is up, and will include information on registration, logistics, and a call for abstracts.

INTERNATIONAL STEERING COMMITTEE
Professor Richard Coffin, Texas A&M University – Corpus Christi, USA
Professor Bjorn Kvamme, University of Bergen, Norway
Stephen Masutani, University of Hawaii, USA
Professor Tsutomu Uchida, Hokkaido University, Japan
Dr. Norio Tenma, National Institute of Advanced Science and Technology, Japan

QUESTIONS?
Please email Mrs. Alessandra Garcia at alessandra.garcia@tamucc.edu

We have arranged a series of workshops since 2000 with the ***main intention to look forward on trends and needs in international research related to hydrates in nature.***

It is a main goal to catalyst international research collaboration which involves industry and academia.

The new trend from Department of Energy, USA, as announced at our 2016 Workshop (June 2016, Honolulu) is that the increase hydrate budgets and 1/3 will be dedicated to international collaboration