CO_2 Hydrate Formation Heat Release as a New Tool to Melt In Situ Methane Hydrates*

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Search and Discovery Article #80089 (2010)
Posted June 30, 2010

*Adapted from oral presentation (by Kirk Osadetz) at AAPG Annual Convention and Exhibition, New Orleans, Louisiana, April 11-14, 2010. Please refer to related article, "Geological Controls of Regional Petroleum Gas Hydrate Occurrence, Beaufort-Mackenzie Basin, Canada," Search and Discovery Article #80076 (2010).

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Abstract

We suggest a new method of the natural gas hydrate exploitation by injection of carbon dioxide into the gas hydrate deposits. The method is based on heating and melting of the natural gas hydrate by the heat released during formation of the carbon dioxide hydrate after CO_2 injection into the natural gas deposit. In Arctic sub-permafrost or offshore the subsurface temperature or sub-bottom temperature are commonly below the stability curves both for natural gas and carbon dioxide hydrates (see Canada; Majorowicz and Osadetz, 2001). In case of CO_2 injection the heat released during the crystallization into CO_2 hydrate warms up the medium, including the natural gas hydrate. In the moment, when the local temperature reaches the stability temperature of the natural gas hydrate (lower than that of the CO_2 hydrate for depths down to some 1km), the temperature stops to increase and the heat from ongoing CO_2 hydrate crystallization is consumed in melting of the natural gas hydrate. The released natural gas can be pumped out. Only when all the natural gas hydrate is melted, does the temperature resume increasing. To secure a safe storage of CO_2 in a form of the solid phase, further CO2 injection must be stopped before reaching the CO_2 hydrate stability temperature. It is shown for a typical case, using the calorimetric equation, that, after CO_2 hydrate formation in about one-fourth of the pore space not occupied by the natural gas hydrate, the released heat is large enough to warm up the whole medium by 5 K at some 0.85 km depth and hence to raise temperature to the melting temperature of the natural gas hydrate. The CO_2 injection into and the CO_2 hydrate formation within the remaining pore space not occupied by the natural gas hydrate can continue, but all the released heat is consumed by the natural gas hydrate melting and the temperature does not increase now. Because the crystallization heats and densities of the natural gas hydrate and of the CO_2 hydrate are similar, the CO_2 hydrate formation in a certain fraction of the pore space will be compensated by the natural gas hydrate decay in another fraction of the pore space of the similar volume. This volume will be available for further CO_2 storage. Therefore, in this case study, it would be possible to melt all the natural gas hydrate (and to pump out all the released natural gas) by injecting carbon dioxide into about 70% of the pore space.

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CO_2 Hydrate Formation Latent Heat Release as a New Tool to Facilitate In Situ Methane Hydrate Dissociation

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COOPERATION: Kirk Osadetz (Natural gas hydrates in Canada) and Fred Wright (CO2 sequestration as hydrates)

Purpose of This Study

- To provide a simple initial model that attempts to characterize the nature of CO_2 hydrate storage in reservoir pore space within, or above a methane hydrate accumulation.

- To predict the effects of the CO_2 hydrate crystallization, especially latent heat effects, both for a hypothetical general case and also at the Mallik site in the Mackenzie Delta on the shore of the Beaufort Sea.

- To model the potential use of CO_2 hydrate latent heat effects as a mechanism for enhancing CH_4 hydrate dissociation (e.g., CO_2 form field gas combustion during production of colocated conventional resources is used to accelerate CH_4 dissociation).

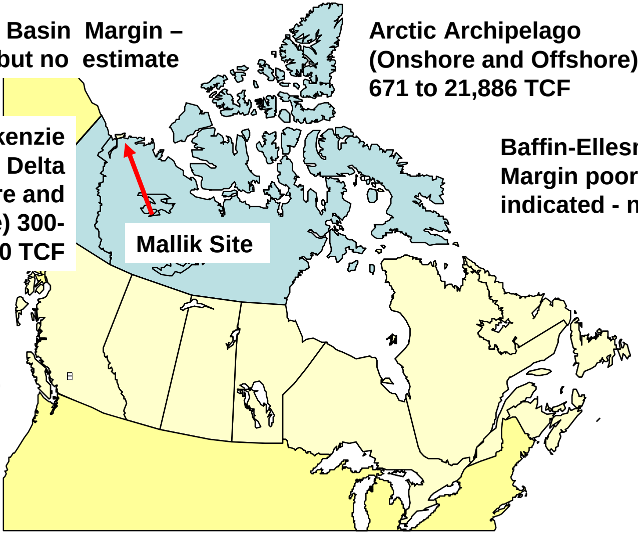
Estimated GH Methane Resources Discounted Stability Zone Volume Method

Amerasian Basin Margin – indicated, but no estimate

Arctic Archipelago (Onshore and Offshore) 671 to 21,886 TCF

Mackenzie Delta (Onshore and Offshore) 300-350 TCF

Baffin-Ellesmere Margin poorly indicated - no estimate



Pacific Margin 113 to 847 TCF

Atlantic Margin 671 to 2,753 TCF

Total in-situ amount of methane in Canadian gas hydrates is estimated to be 1,553 to 28,593 TCF (0.44 to 8.1 x 10^{14} m^3), as compared to a conventional Canadian gas potential of ~953 TCF (0.27 X 10^{14} m^3).

Presenter's Notes:

Canada is an Arctic and marine nation, and gas hydrates (GH) are confirmed or inferred to occur widely in its continental margins and permafrost regions. The total in-situ amount of methane in Canadian gas hydrates is estimated to be 1,553 to 28,593 TCF (0.44 to 8.1 x 10^{14} m^3), as compared to a conventional Canadian gas potential of ~953 TCF (0.27 X 10^{14} m^3). The geographic distribution of Canadian gas hydrates is:

Region ; Imperial Measure ; Metric Measure

Mackenzie Delta–Beaufort Sea ; 300 to 350 TCF ; 8.82 to 10.23x10^{12} m^3 *Arctic Archipelago ; 671 to 21,886 TCF; 0.19 to 6.2 x* 10^{13} m^3

Atlantic Margin ; 671 to 2,753 TCF ; 1.9 to 7.8 x 10^{13} m^3

Pacific Margin ; 113 to 847 TCF; 0.32 to 2.4 x 10^{13} m^3

Gas hydrate accumulations are also identified in Alaska and the offshore U.S.A. This suggests that gas hydrates represent a potential future assurance of North American natural gas supply, if the gas can be recovered economically.

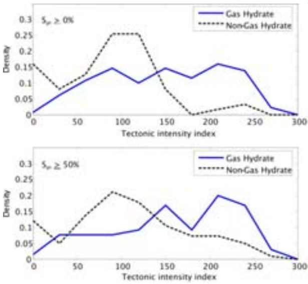
BMB GH are associated with structure and conventional petroleum accumulations

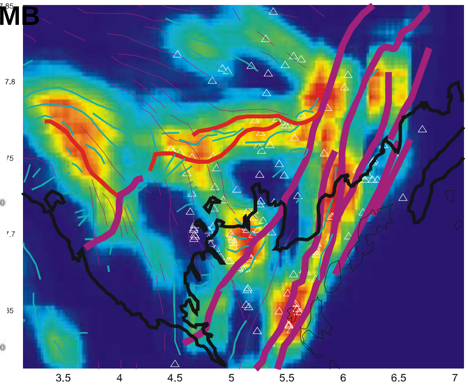
- GH rarely occur within the IBP (except Taglu).

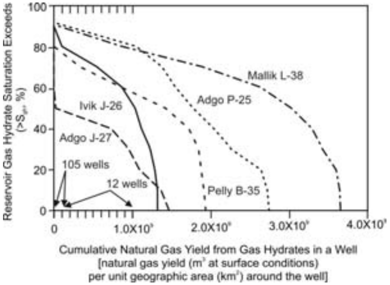
- A gap is common between base IBP and top of GH, which usually occurs below a geological ‘seal’.

- GHs are strongly associated with occurrences and features of the conventional thermogenic petroleum systems.

Tectonic Intensity BMB







The BMB GH yield occurs predominantly in a few wells (i.e., it is unevenly distributed like the conventional resource).

Presenter's Note:

BMB=Beaufort- Mackenzie Basin; IBP=Ice-Bearing Permafrost.

Mallik Gas and Gas Hydrate Field

- Currently the best and most intensively characterized GH site globally.
- Among the most concentrated gas hydrate reservoirs:
  - >200 m gross hydrate thickness;
  - High gas hydrate concentrations.
- Transparent to industrial seismic, but no geological risk.
- Extensive engineering, geological and geophysical knowledge.
- Physical reservoir conditions similar to deposits offshore Japan.
- An accessible onshore location for experiments.

At Mallik the GH resource (~4 Tcf) is ten times the conventional gas reserve (~400 BCF).

Presenter's Notes:

Gas hydrates occur extensively within Canada's Mackenzie Delta, Beaufort Sea Basin and in the Arctic Islands, both onshore and offshore. Many of the subsea gas hydrates here are actually thick relics of the last time when sea level was lowered by water being locked up in the continental ice sheets. The reason that these gas hydrates are of immediate interest to us is because of their opportunity to augment the production of natural gas in the Mackenzie Delta, which is the site of the a proposed major pipeline project. The details of gas hydrates occurrence in the Mackenzie Delta have been actively investigated by an international group of researchers led by Scott Dallimore at the Mallik Bay Gas Hydrate Research Well.   Why go to the Mallik Research Site? First, Mallik is a great place to look for gas hydrates. Since Imperial Oil first encountered them in the early 1970's, they've been well characterized and the Geological Survey of Canada and the Japan National Oil Corporation went there subsequently in 1998. We know that there are over two hundred metres of gross gas hydrate thickness within the rock layers. There are very high concentrations of gas within the gas hydrates there, up to ninety percent of the cages are filled with gas in the hydrates. There's extensive engineering and geophysical data from the site because of the number of wells that have been drilled there and the other scientific investigations.

Mallik Gas Hydrate Research Campaigns

- 1972 – Imperial Oil L-38 well discovery, recognition and a short test of the Mallik GH accumulation.

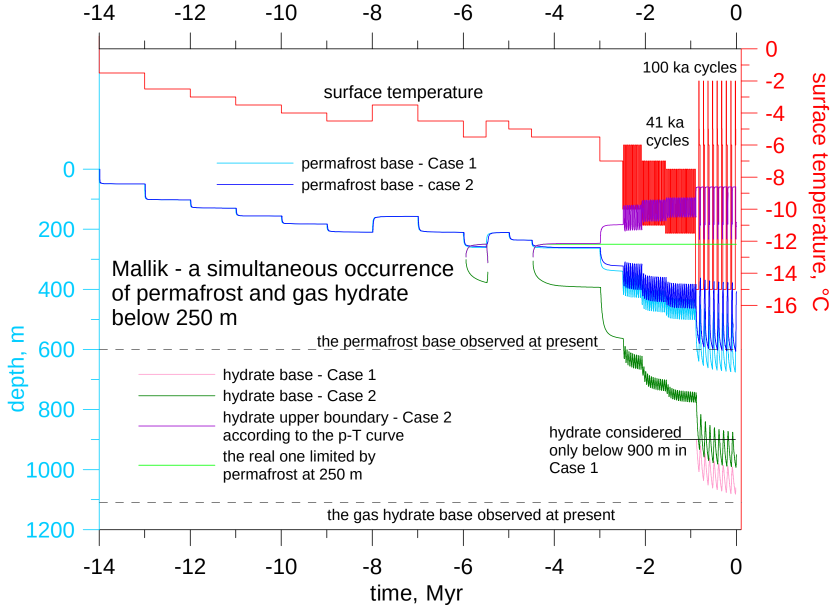
- 1998 – 2L-38 research well to characterize and core the GHSZ and GH-bearing intervals.

- 2002 – 3L-38, 4L-38 and 5L-38 research wells to core, characterize and test (MDT and thermal stimulation) GH reservoir in the 5L-38 well.

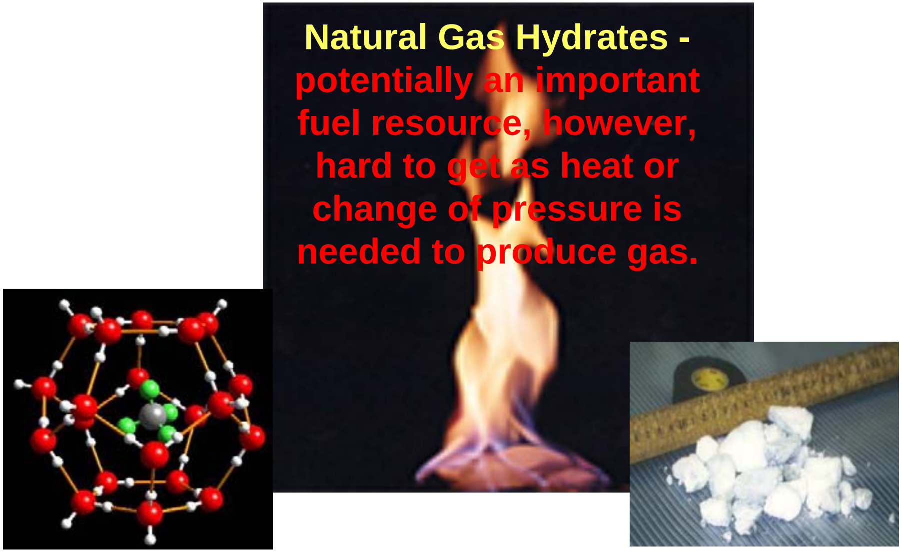
- 2007-08 – additional characterization and two short production tests of re-entered and deepened Mallik 2L-38 and 3L-38 wells.

Case 2, gas hydrate forms dynamically

- Interfingering occurrence of permafrost and gas hydrate below 250 m is not observed generally.
- Dynamic formation lower thermal conductivity resulting in a higher temperature gradient that moves the permafrost and hydrate bases upward, above their present observed positions.



Natural Gas Hydrates - potentially an important fuel resource, however, hard to get as heat or change of pressure is needed to produce gas.



McGrail et al., (2007) propose replace CH_4 hydrate by CO_2 hydrate by injecting a CO_2 and water emulsion at temperatures (+15 °C) higher than the temperature of the CH_4-hydrate bearing reservoir (+2 °C) to facilitate (suitable for marine settings – a challenge in the Arctic) *

*McGrail, B. P., H. T. Schaef, M. D. White, T. Zhu, A. S. Kulkarni, R. B. Hunter, S. L. Patil, A. T. Owen, and P. F. Martin. 2007. *Using Carbon Dioxide to Enhance Recovery of Methane from Gas Hydrate Reservoirs: Final Summary Report.* PNNL-17035, Pacific Northwest National Laboratory, Richland, Washington.

Presenter's Notes:

Because the two most common host molecules are significant GHG's, the role of GHs as a reservoir for GHG's is important.

Naturally occurring gas hydrates natural clathrates, or "ice-like" crystalline mixtures of water, "host", and gas, "guest", molecules. There are three common hydrate crystal structures. Structure I, the predominant natural form, accommodates small (0.4–0.55 nm) guest molecules, typically methane. Structure II accommodates larger (0.6–0.7 nm) guest molecules, including heavier hydrocarbons. Structure H can host mixtures of both small and large (0.8–0.9 nm) guest molecules. Methane and carbon dioxide are common guests because of availability and their thermodynamic stability in permafrost subsurface and marine environments. There is a variety of other 'guest' molecules including nitrogen and hydrogen sulphide.

Gas hydrates are: a potential petroleum resource, a transportation, geotechnical and seafloor hazard, a postulated agent of global change, and a medium for industrial processes – especially transportation and purification. The efficient storage of natural gas, up to 164 volumes per volume of gas hydrate, results in an unconventional gas reservoir comparable to a conventional reservoir at 16 MPa. Cage sizes induce compositional fractionation, since other ions and compounds are excluded as the hydrate forms. This impacts gas composition and it is the basis for hydrate process technologies. Finally, the positive dissociation enthalpy required to liberate natural gas controls both reservoir energetics, during in-situ production, and the "self-preservation" effect that permits intercontinental transportation of gas hydrate pellets.

CO_2 and CH_4 hydrate stability conditions are overlapping in sub-permafrost areas

Perhaps the latent heat effects of CO_2 hydrate formation can be used directly to facilitate Arctic methane hydrate production?

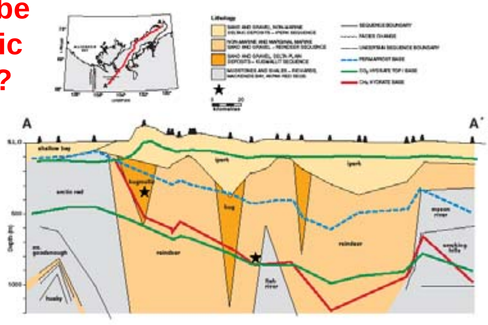
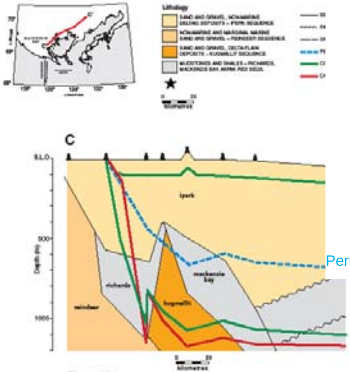


Figure 16



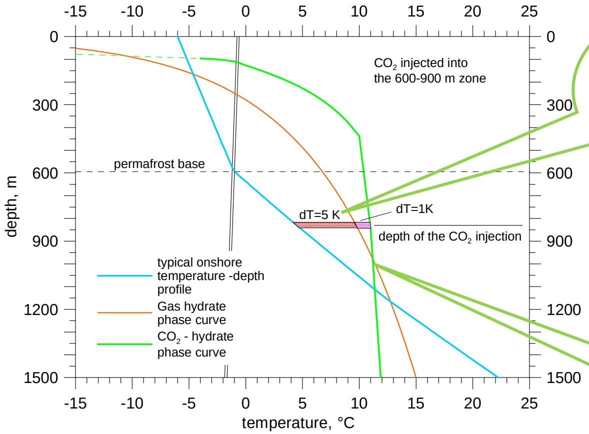
Permafrost base

CO2 hydrate stability base

CH4 hydrate stability base

Figure 18

Formation of CO_2 hydrates in methane hydrate intervals releases latent heat



In assumed general permafrost area case the temperature at the depth of the CO_2 injection is 5 K below the natural gas hydrate stability curve and 6 K below the CO_2 hydrate stability.

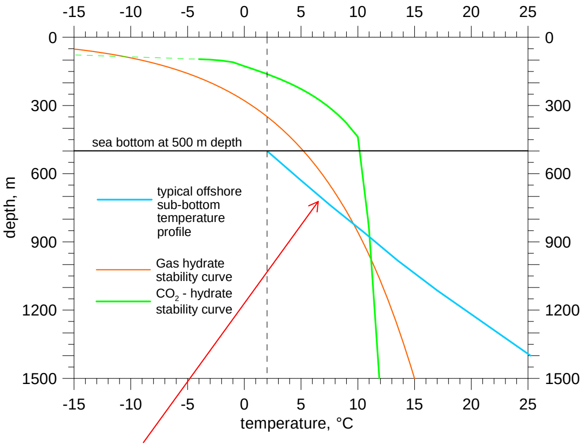
CH4 & CO2 hydrates phase curves intercept at the ~ 1km

Heat balance calculations show that the heat of crystallization of CO_2 hydrate formation in about a quarter of the pore space, not occupied by the natural gas hydrate, is large enough to warm the Earth volume by 5 K and provide sufficient heat to dissociate the available methane hydrates.

Presenter's Notes:

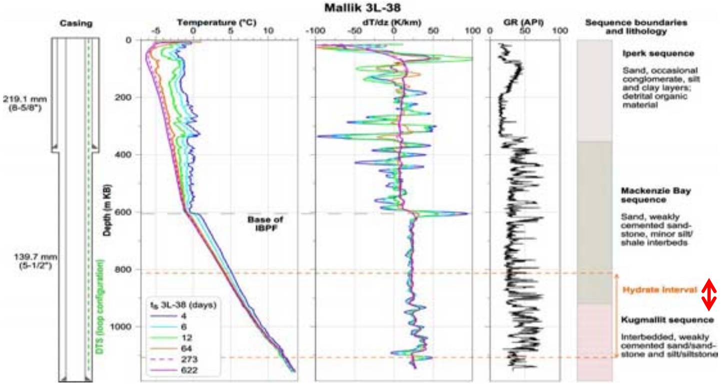
This is general case for a typical case of 60mW/m2-deep heat flow in the area with deep 0.6km-thick permafrost.

Direct Injection: the Offshore Case



The sub-sea floor temperature profile is below the stability curves both of natural gas and carbon dioxide hydrates over a large (~400 m) interval.

Direct injection: the Mallik case



- •Methane hydrate occurs >0.8km only.
- •The only interval, where CO2 injection leads to immediate methane hydrate dissociation is in 0.8 – 1km since the two hydrate stability curves intersect at ~1km

if CO_2 can be injected only into the pore space not occupied by gas hydrate, then the latent heat of crystallization will be enough to melt about 55% of the natural gas hydrate and the formation temperature stays at the natural gas hydrate phase curve.

Simulated time changes of the subsurface temperature

is done by numerical solving the transient heat conduction equation (Safanda et al., 2004):

$$C_v \; \partial T/\partial t = \partial[K(\partial T/\partial z)]/\partial z + A \qquad (1)$$

T -temperature, *K* - thermal conductivity, C_v - volumetric heat capacity, *A* - heat generation, *z* -depth, *t* - time.

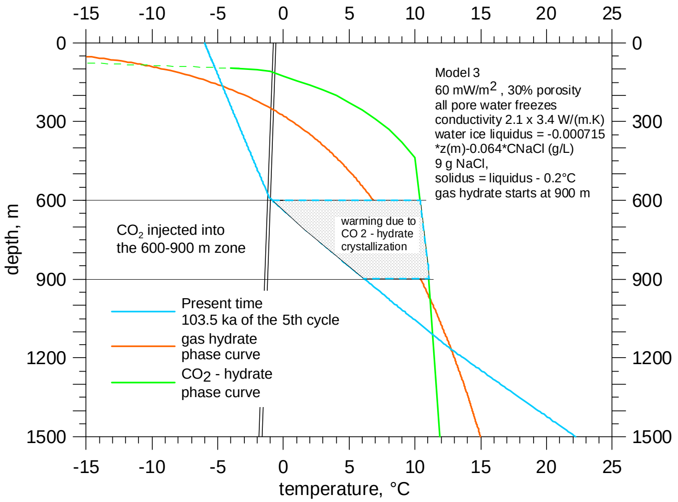
The finite-difference scheme of equation (1) on the depth and time grids $..z_{k-1}$, z_k , z_{k+1} ,... and $...t^n$, t^{n+1} ,....., respectively, has a form:

$$C_{v,k}{}^n (T_k{}^{n+1} - T_k{}^n) / (t^{n+1} - t^n) = 2K_{k+1}{}^n (T_{k+1}{}^{n+1} - T_k{}^{n+1})/[\Delta z_{k+1}(\Delta z_k + \Delta z_{k+1})] -$$
$$2K_k{}^n (T_k{}^{n+1} - T_{k-1}{}^{n+1})/[\Delta z_k(\Delta z_k + \Delta z_{k+1})] + A_k$$

where the subscript *k* and the superscript *n* denote values at the *k*th depth step and the *n*th time step, respectively; $\Delta z_k = z_k - z_{k-1}$; $K_{k+1}{}^n = \Delta z_{k+1} / [\int_{z_k}^{z_{k+1}} dz/k^n(z)]$.

The difference scheme together with the upper and lower boundary conditions lead to a system of difference equations for unknown values $T_{k-1}{}^{n+1}$, $T_k{}^{n+1}$, $T_{k+1}{}^{n+1}$, with a tridiagonal matrix, which can be solved by the forward method (Peaceman and Rachford, 1955).

CO_2 storage sub-permafrost without CH_4 hydrate



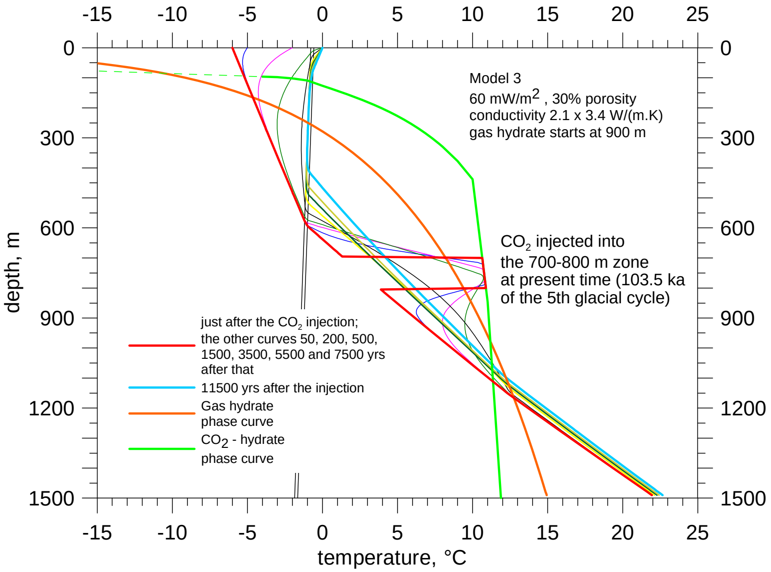
Initially, the injected CO_2 freezes immediately, because the surrounding temperature is below its freezing point. Subsequently, the latent heat of crystallization warms up the Earth.

The latent heat effect is huge (429.66 kJ/kg * 910 kg/m3 * 0.18 = 0.704E8 J/m^3) .

Before injecting the available storage volume (60% saturation of the pore space, porosity 30%, i.e., 18% of the total volume) the temperature increases above CO_2 hydrate stability and injected CO_2 remains unfrozen.

CO_2 storage sub-permafrost above CH_4 hydrate

Carbon dioxide injection into the 700-800 m zone above methane hydrate



Temperature-depth-time dynamics after CO2 injection into a 700-800m zone.
Note cooling of the zone of injection and warming of the zones above (permafrost) and below (CH4 hydrate).

Key Model Results

- If CO_2 is injected only into the water wet pore space of methane hydrate accumulations the latent heat of crystallization melts ~55% of the methane hydrate without significantly increasing the temperature above methane hydrate stability.
- If CO_2 is injected into water wet pore space of methane hydrate accumulations near BGHSZ, then the injection of CO_2 equal to 63% of the total pore space volume releases sufficient heat to dissociate all the methane hydrate. Continued CO_2 injection results in a warming of the CO_2 hydrate phase toward its own stability limit.
- If methane hydrate occurs deep in the GHSZ (>0.8km as at Mallik), then directly injected CO_2 causes immediate methane hydrate dissociation in the interval ~0.8-1 km only as methane and CO_2 hydrate stability curves intersect at the ~1 km depth.
- If CO_2 is injected into a zone above ~0.8km heat transport to the underlying methane hydrate causes subsquent dissociation (in matter of years).