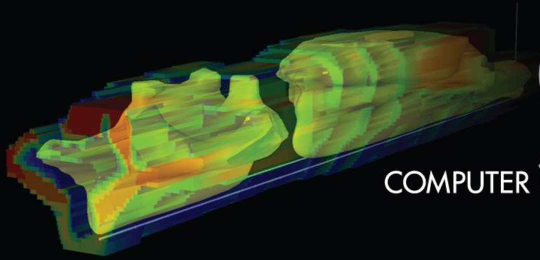

第62期：使用STARS模拟天然气水合物

Methane Hydrates: A Major Energy Source for the Future or Wishful Thinking?

Gas Hydrate simulation using STARS

Contents:

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- Introduction to gas hydrates- why, what and where?
- Global distribution of hydrates and conceptual production techniques.
- Phase behavior of gas hydrates.
- Kinetics of formation and dissociation of hydrates.
- Gas hydrates in porous media- distribution, permeability in presence of hydrates etc.
- Mathematical models for hydrate formation and dissociation.
- Experimental vs. simulation results.
- Hydrate simulation in STARS?
- Simulation examples.

Natural Gas Hydrates

- Gas hydrates as lab curiosity.
- A nuisance in the process facilities and pipelines.
- Now looked as potential future source of energy.

What are Gas Hydrates

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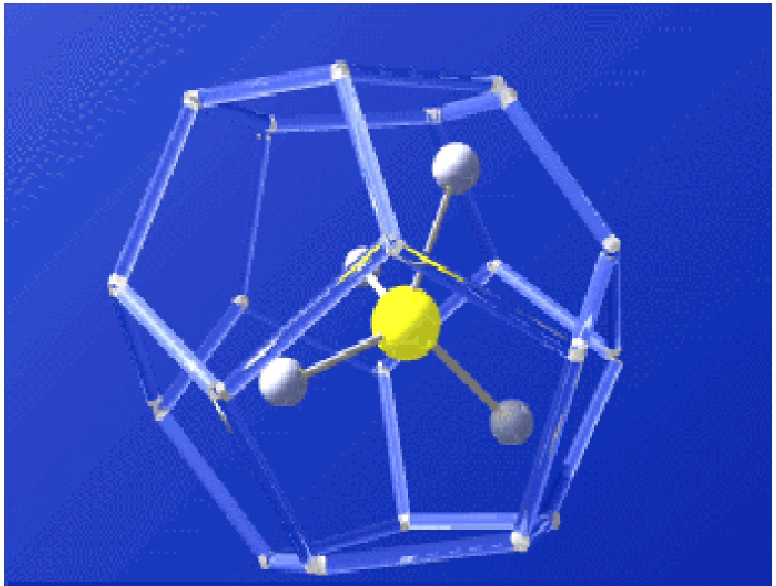
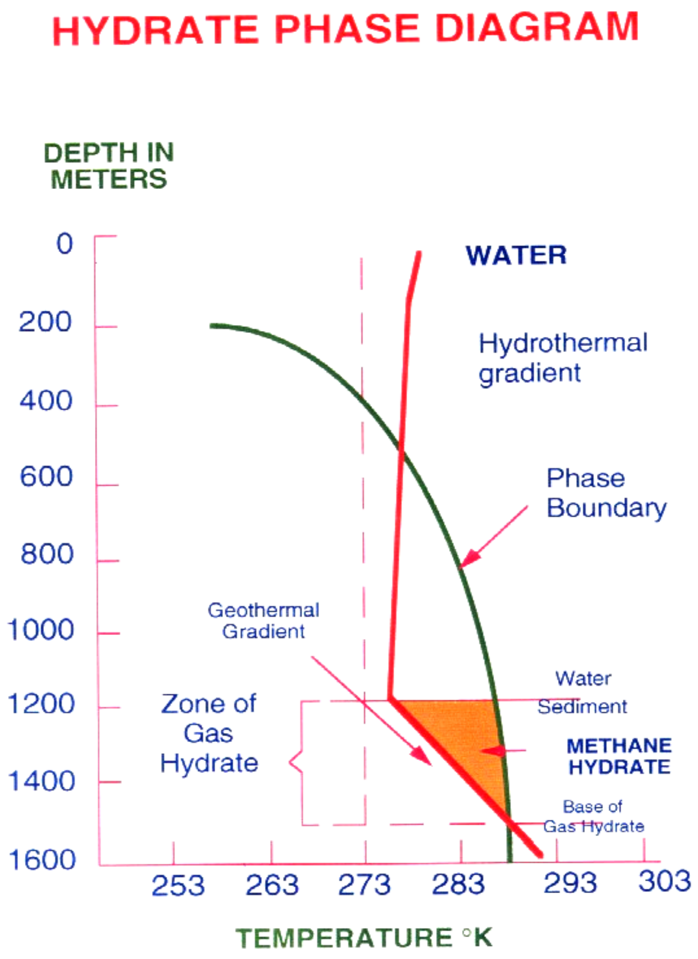
Naturally occurring crystalline substances composed of water and gas in which a solid water-lattice accommodates gas molecules in a cage like structure



Hydrate structure showing carbon (center) and hydrogen (attached to center) trapped in ice lattice. (Source: USGS)

Formation - Parameters

- Low Temperature
- High pressure
- Gas and water composition



Why gas Hydrates?

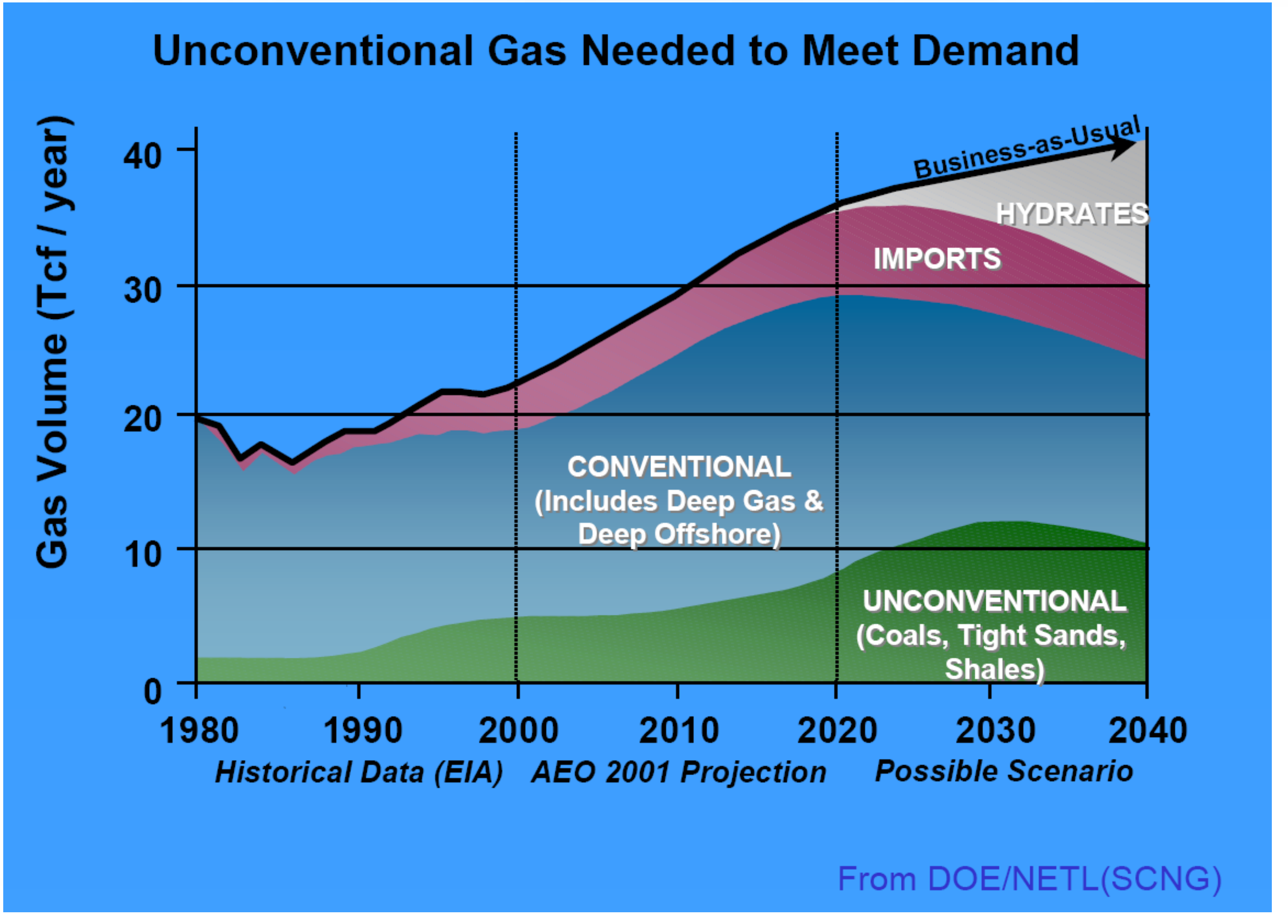
- Growing energy supply demand gap.
- Depleting conventional petroleum resources.
- Potential source of clean fuel for the future.
- Sea-floor stability & drilling safety
  - – Ensure safety of deepwater oil and gas recovery through or near marine hydrate sediments
- Global climate impact
  - –The role of natural hydrate in global climate and deep sea life
- Production problems
  - –Pipeline flow assurance

Why gas Hydrates?

- Worldwide estimate of methane in methane hydrates:
  - ~ 700,000 Tcf[20,000 trillion cubic meters]
  - ~ Conventionally recoverable methane –8,800 Tcf [250 trillion meters]
  - ~ two times total energy in coal, oil and conventional gas

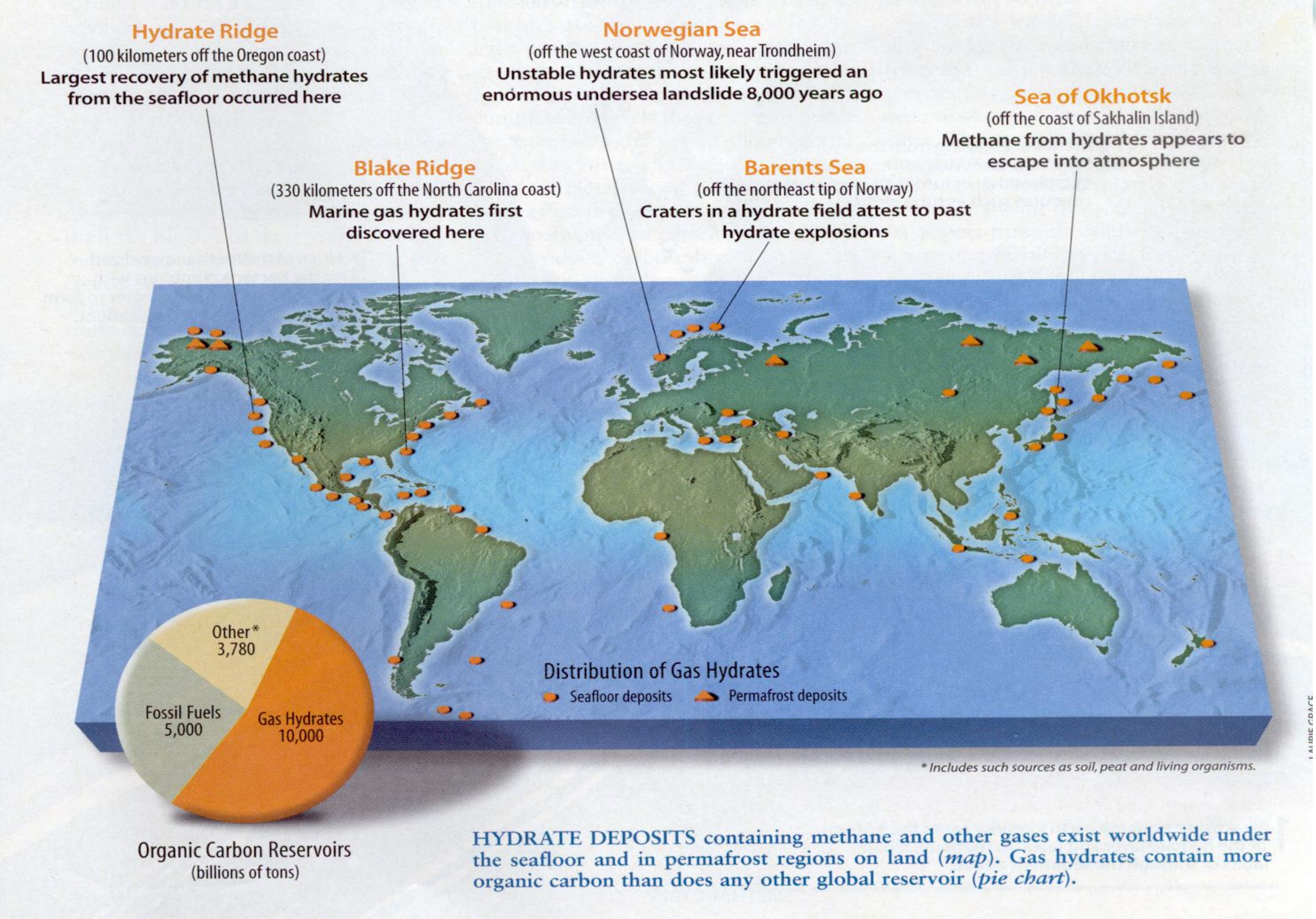
- United States estimate of methane in methane hydrates:
  - ~ 200,000 Tcf gas-in-place in hydrates (38,000 TcfGOM)
  - ~ Remaining technically recoverable natural gas - 1,400 Tcf

Why gas Hydrates?



From DOE/NETL(SCNG)

Global Distribution of Gas Hydrates



Hydrate Ridge
(100 kilometers off the Oregon coast)
Largest recovery of methane hydrates from the seafloor occurred here

Norwegian Sea
(off the west coast of Norway, near Trondheim)
Unstable hydrates most likely triggered an enormous undersea landslide 8,000 years ago

Sea of Okhotsk
(off the coast of Sakhalin Island)
Methane from hydrates appears to escape into atmosphere

Blake Ridge
(330 kilometers off the North Carolina coast)
Marine gas hydrates first discovered here

Barents Sea
(off the northeast tip of Norway)
Craters in a hydrate field attest to past hydrate explosions

Organic Carbon Reservoirs
(billions of tons)

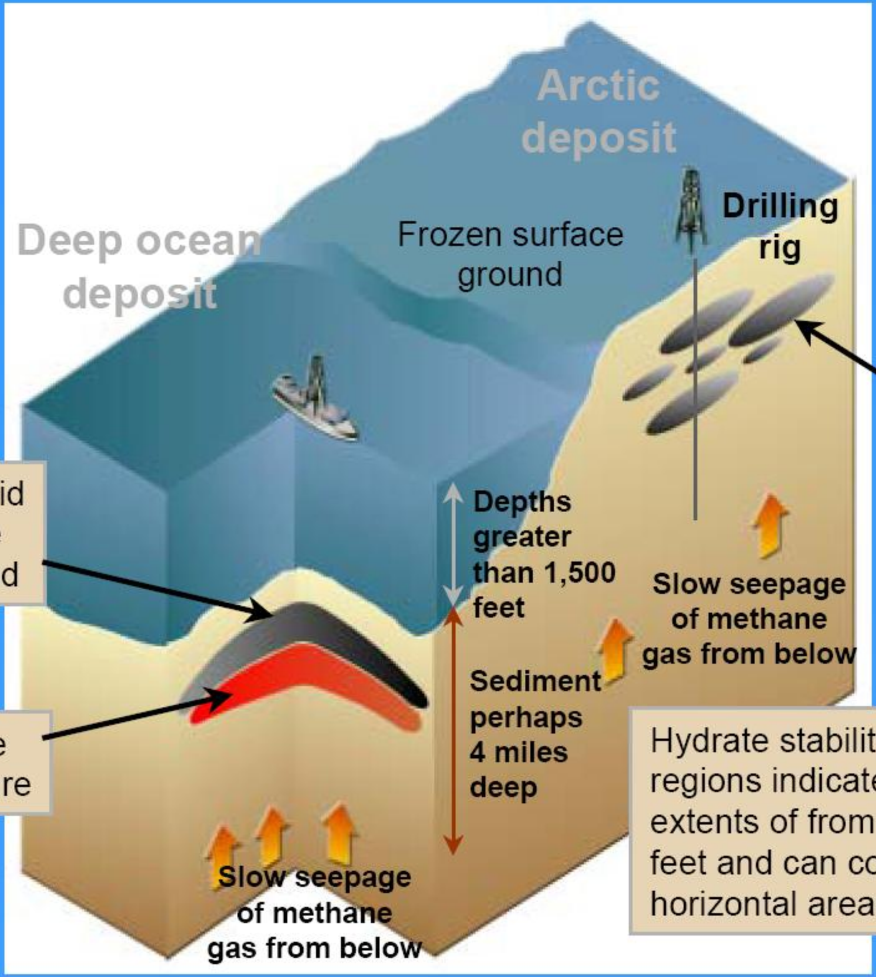
* *Includes such sources as soil, peat and living organisms.*

HYDRATE DEPOSITS containing methane and other gases exist worldwide under the seafloor and in permafrost regions on land (*map*). Gas hydrates contain more organic carbon than does any other global reservoir (*pie chart*).

Gas hydrate volume balance

1 M^3 Gas hydrate → 164 M^3 gas + 0.8 M^3 of water

Types of Methane Hydrate Deposits



Impermeable solid methane hydrate embedded in mud

Trapped methane gas under pressure

Solid methane hydrate ice forms in bands and lenses close to bitterly cold surface

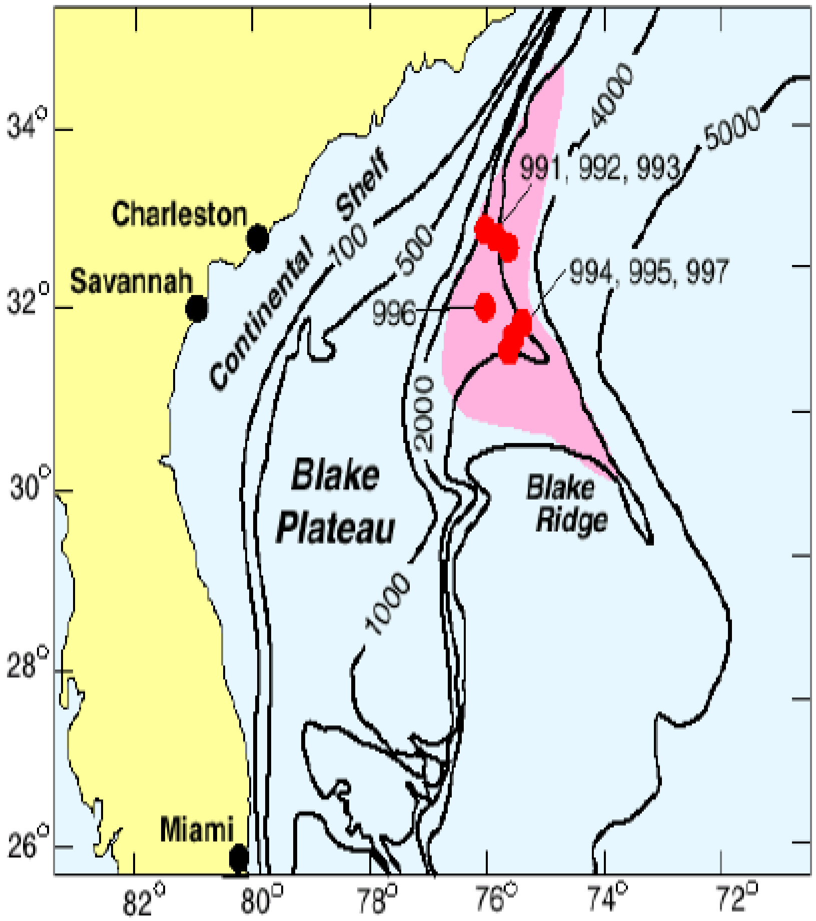
Hydrate stability zone regions indicate vertical extents of from 1,000-2,000 feet and can cover large horizontal areas

From DOE/NETL(SCNG)

How have hydrate accumulations been assessed?

- Small portion of evidence for hydrate accumulations is from direct sampling
- Mostly inferred from other sources
    - seismic reflections
    - well logs
    - drilling data
    - pore-water salinity data

Blake Ridge Hydrate Occurrence



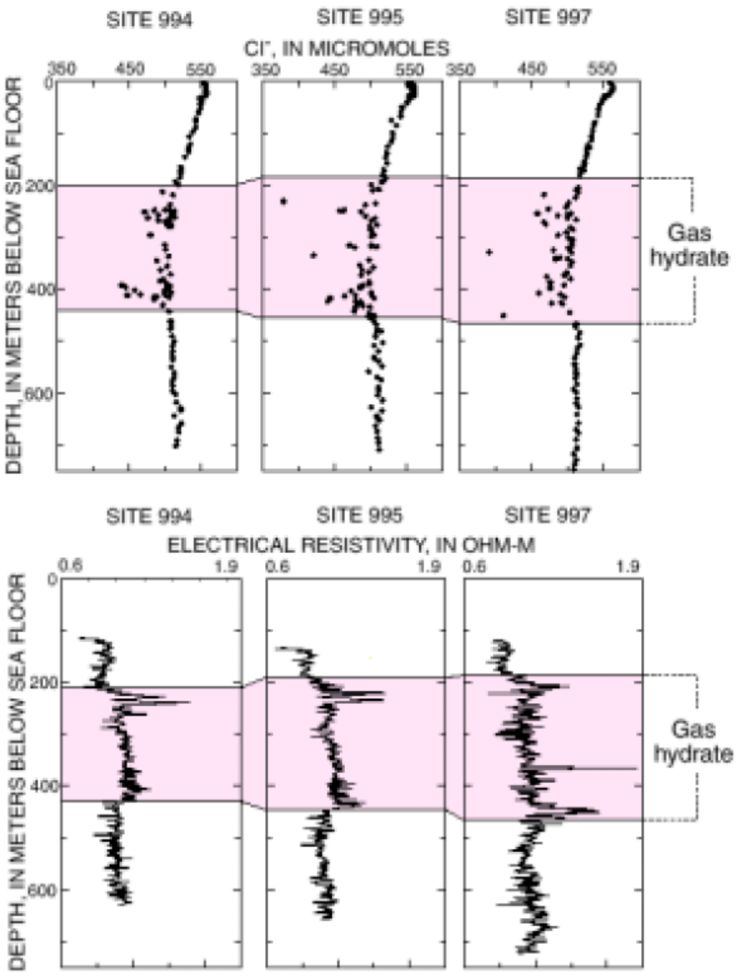
Courtesy Collett USGS

❖Seismic profiles marked by bottom-simulating reflectors (BSRs) along Atlantic margin of US

❖Water depths -2,000 to 4,800 meters

❖Methane hydrate stability zone from 0 to 700 meters

Blake Ridge



Courtesy Collett USGS

❖**Hydrates disseminated within interval from 190 to 450 mbsf**

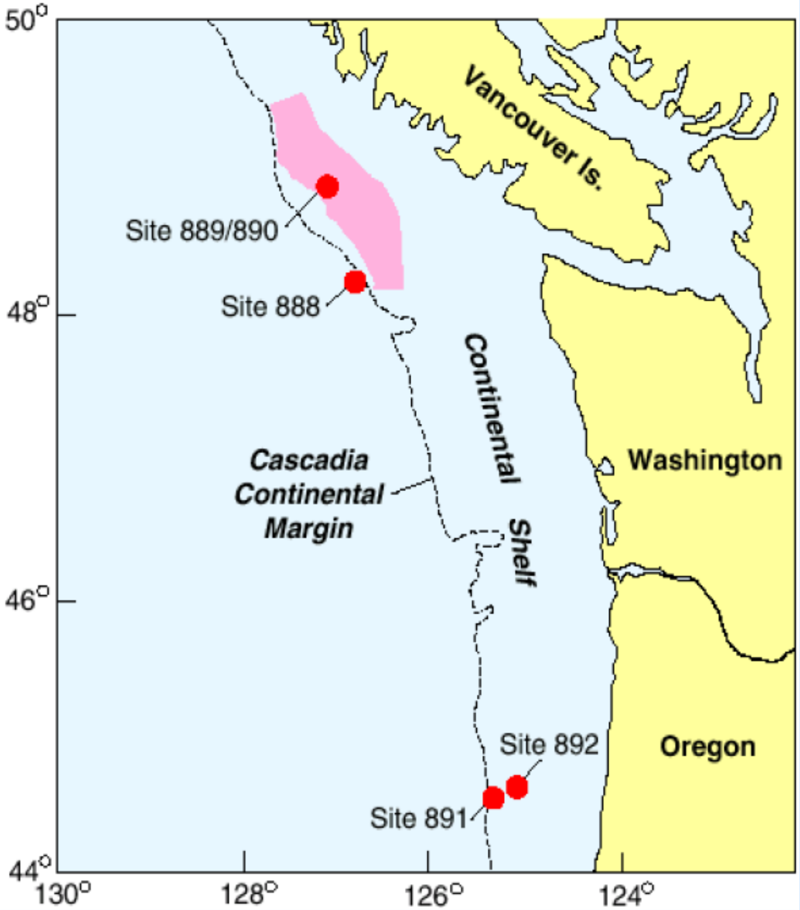
❖**Hydrate saturations inferred from interstitial water chloride data and log data**

❖**Estimated maximum hydrate saturation**

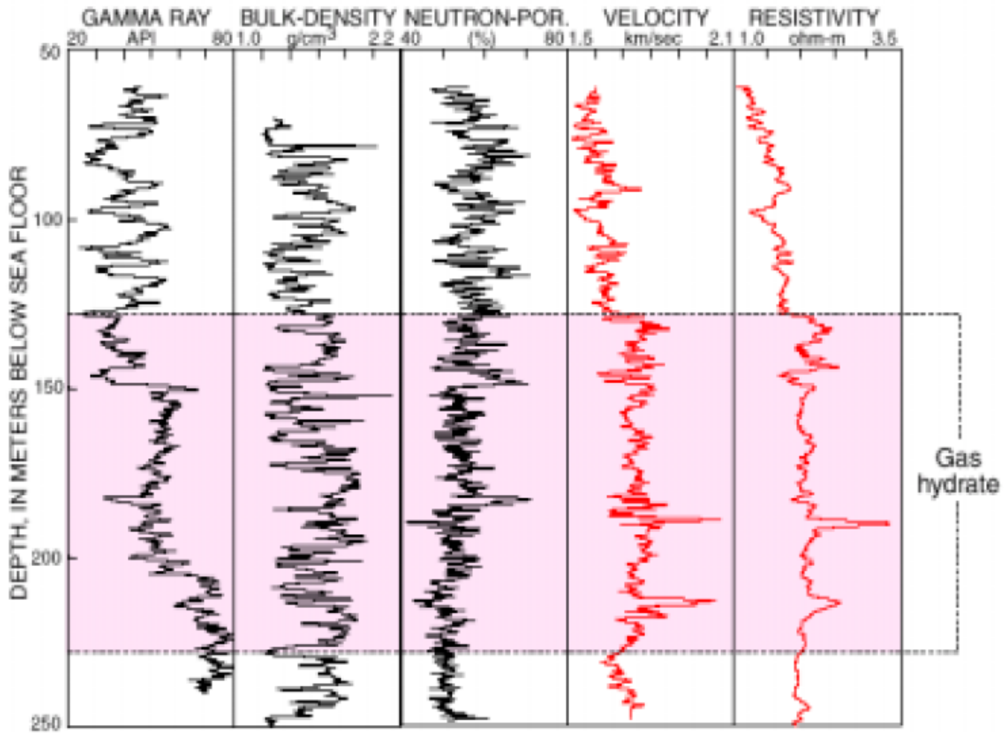
- **−7% in Hole 994**
- **−8.4% in Hole 995**
- **−13.6% in Hole 997**

❖**Hydrate saturation in ocean sediments about 4 to 6 % average.**

Cascadia Continental Margin Occurrence

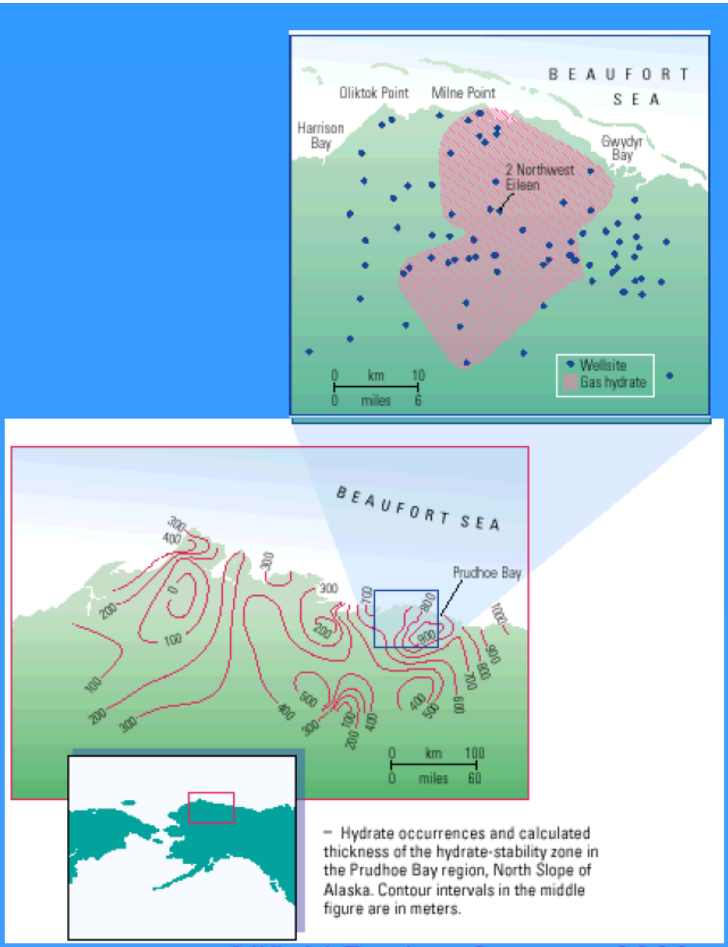


Site 889 - Inferred hydrates saturation: 5% to 39%



Courtesy Collett USGS

Prudhoe Bay-Kuparuk River Area in Alaska



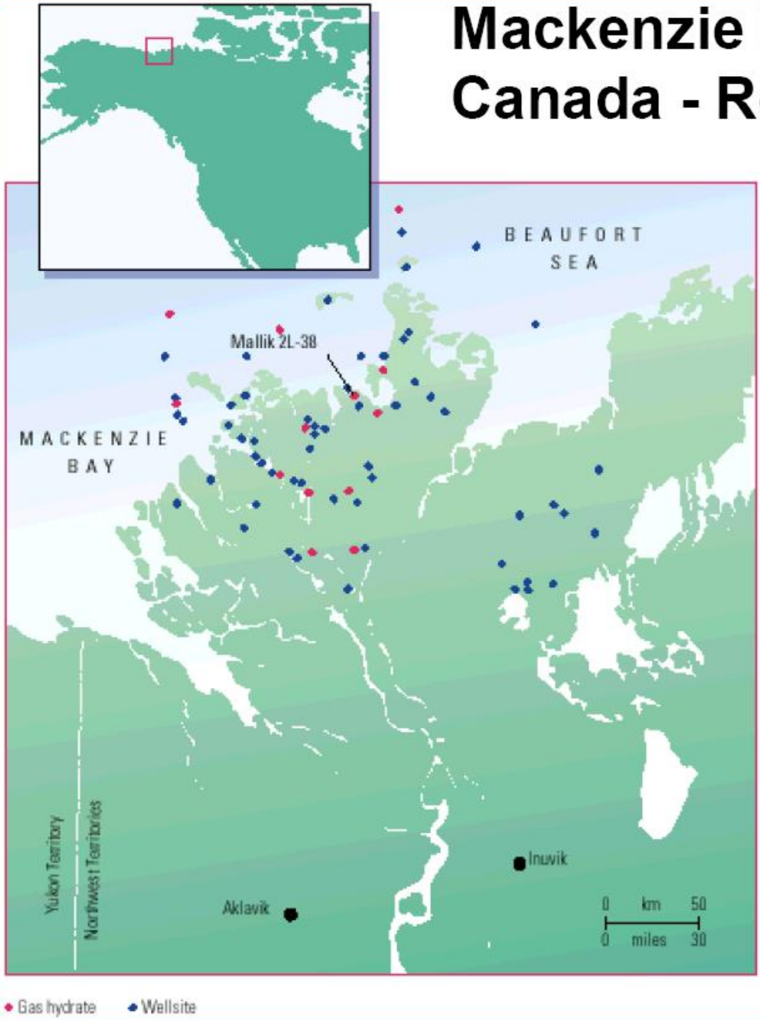
– Hydrate occurrences and calculated thickness of the hydrate-stability zone in the Prudhoe Bay region, North Slope of Alaska. Contour intervals in the middle figure are in meters.

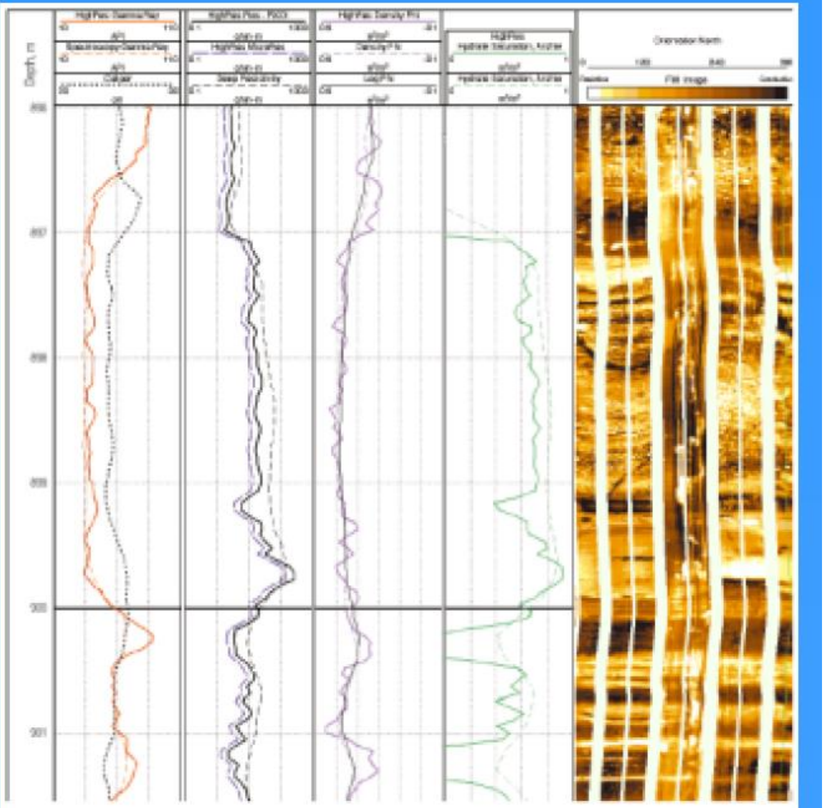
Oilfield Review Summer 2000

Prudhoe Bay-Kuparuk River Area in Alaska

- 1972 - Gas hydrates recovered in pressure core from 2 NW Eileen
- Thickness of gas-hydrate stability zone - 210 to 950 m [690 to 3120 ft]
- 50 North Slope wells revealed hydrates in six zones (Collett USGS)
- 1.0 to 1.2 trillion cubic meters [35 to 42 Tcf]

Mackenzie Delta, Northwest Territories, Canada - Research Well Mallik 2L-38





– Well logs and images from the top few meters of the hydrate layer in the Mallik 2L-38 well. The resistivity in Track 2 shows an increase indicative of hydrocarbon. Computed hydrate saturation in Track 4 reaches more than 80%.

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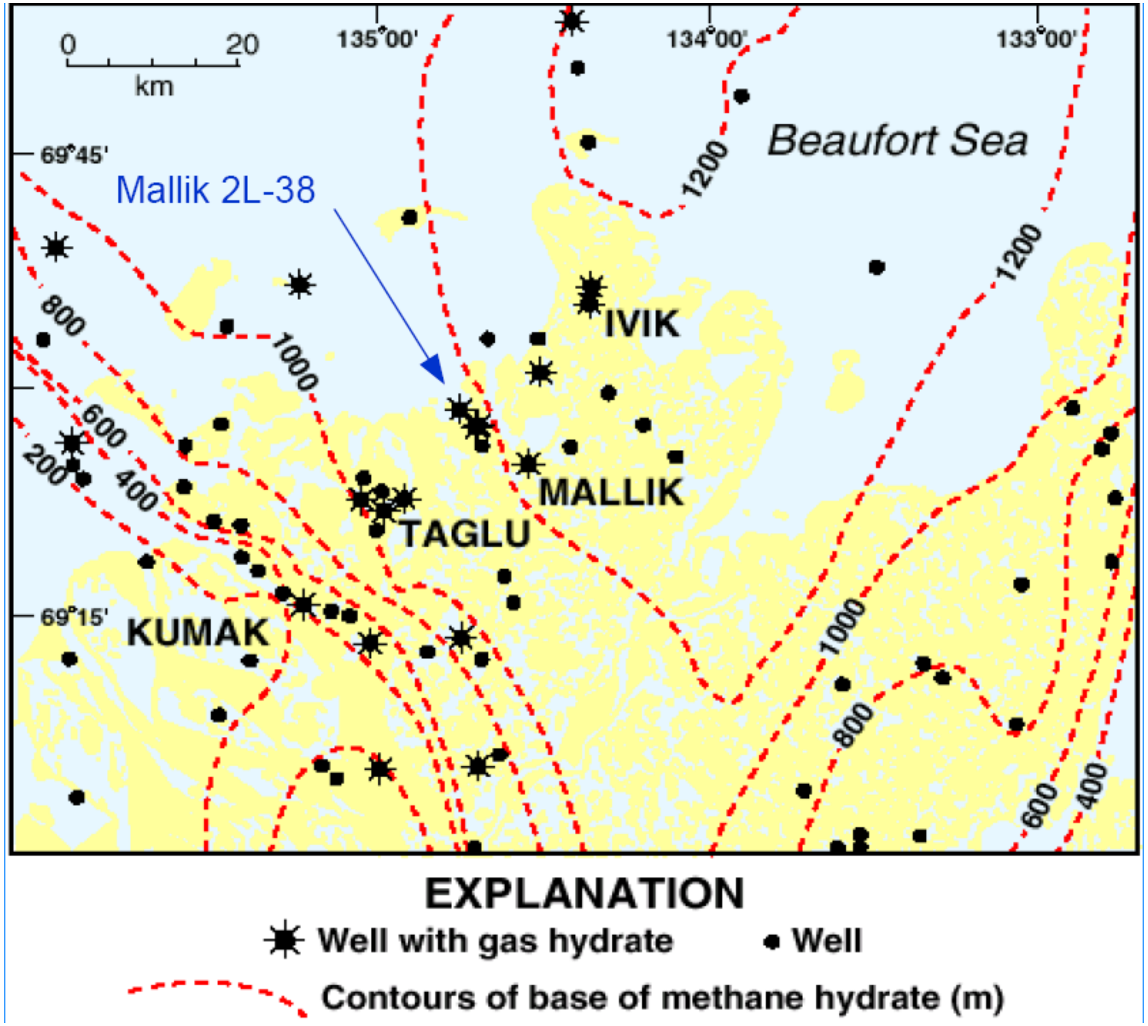
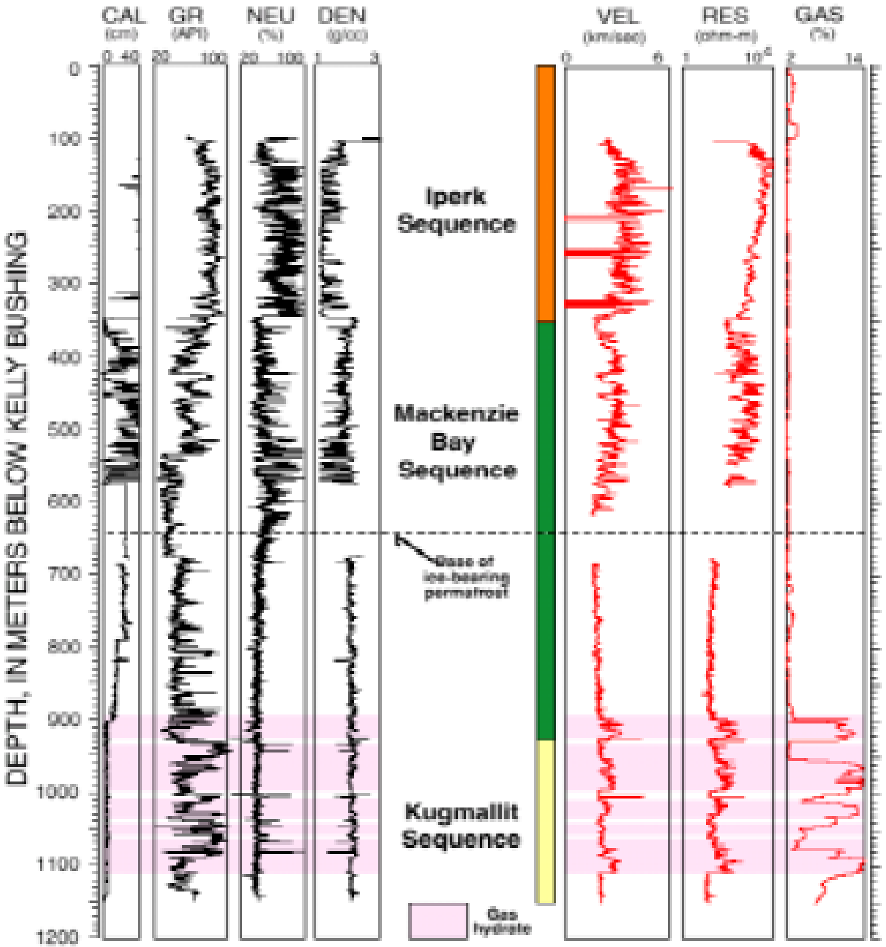
Mackenzie Delta, Northwest Territories, Canada



Inferred hydrate in 25 wells



Mackenzie Delta Mallik2L-38

- ❖37 m core from 878 to 944 m
- ❖Wellbore images and core indicate high quality sandstone
- ❖Well log inferred gas hydrate from 890 to 1100 m
- ❖20 to 40% porosity
- ❖Archie calculated saturation – up to 90%

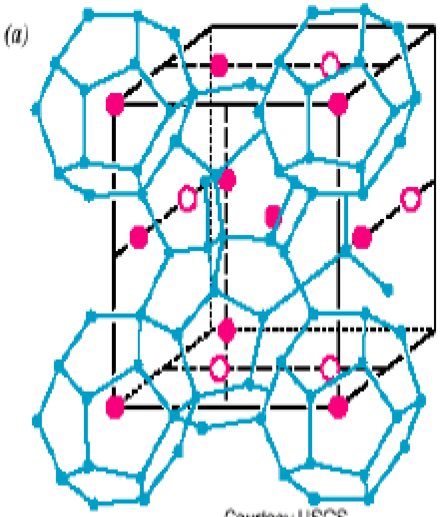
Offshore Japan Nankai -Trough

– Regions with bottom-simulating seismic reflections offshore Japan.

Oilfield Review Summer 2000

- Dozen areas identified by BSRs
- Exploratory well drilled in 1999/2000 in 945 m of water
- Main well drilled to 3300 m
- Cored and logged
- Maximum gas-hydrate saturation estimated at about 80%.

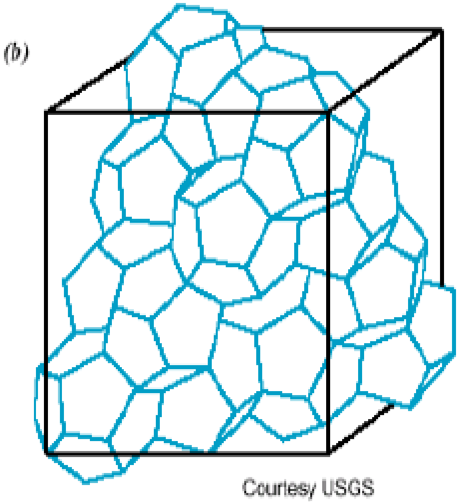
Methane Hydrates Structure



Courtesy USGS

Structure I

Methane, Ethane, Carbon dioxide, etc.



Courtesy USGS

Structure II

Propane, Iso-butane, etc.

Sloan, “Clathrate Hydrates: The Other Common Solid Water Phase,”Ind. Eng. Chem. Res. 2000, 39, 3123-3129)

Phase boundary

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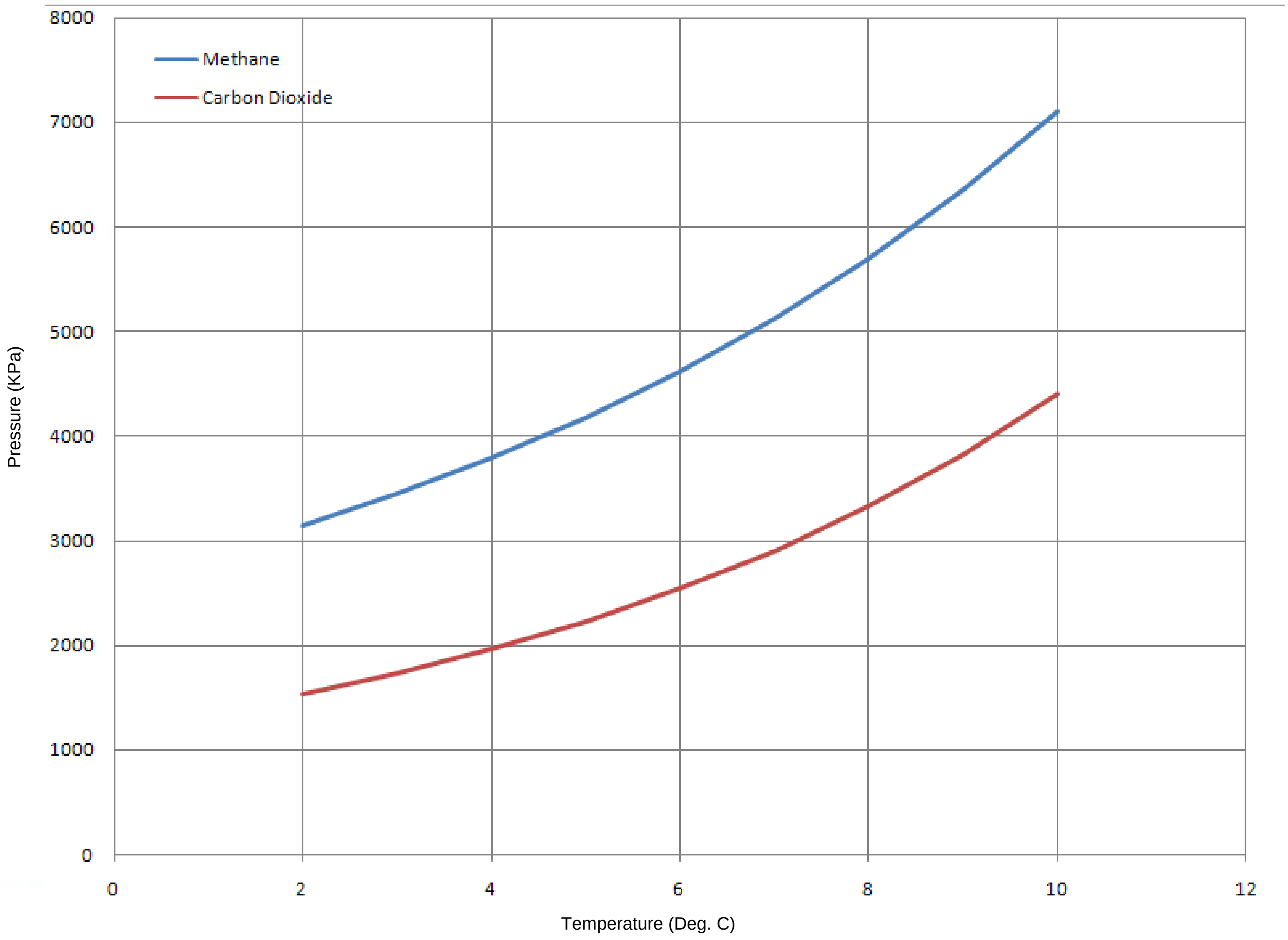
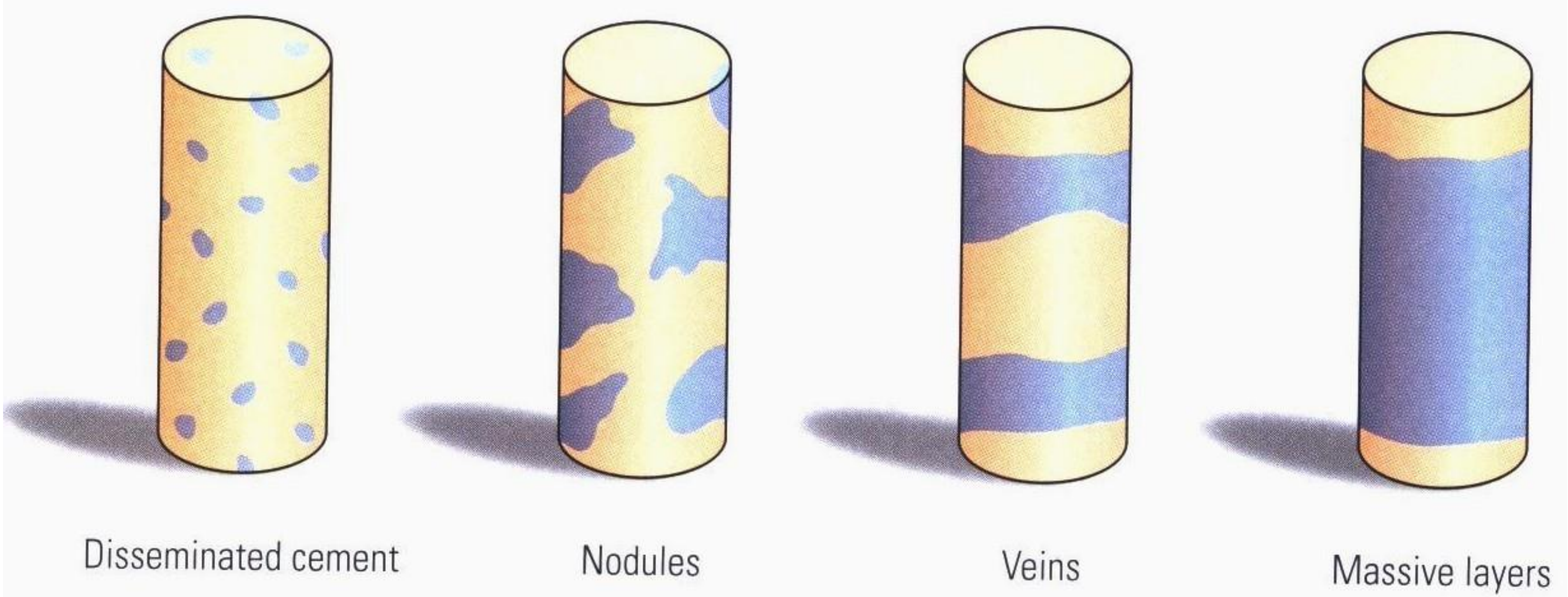
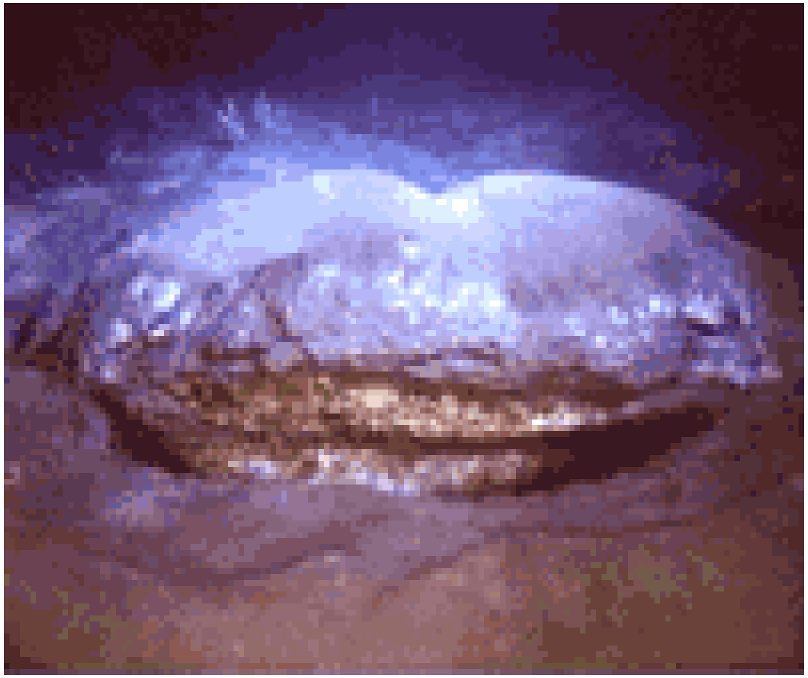


Distribution of hydrates in sediments

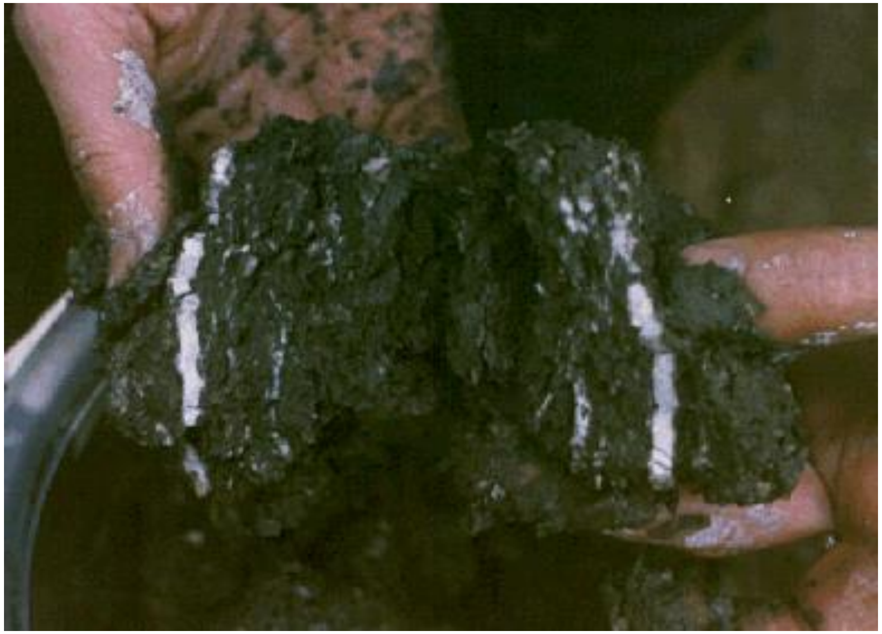


^ How hydrate is distributed in sediments. A formation can contain *(left to right)* hydrate as disseminated cement, nodules, veins and massive layers.

Natural gas hydrates



Hydrate mound on seafloor



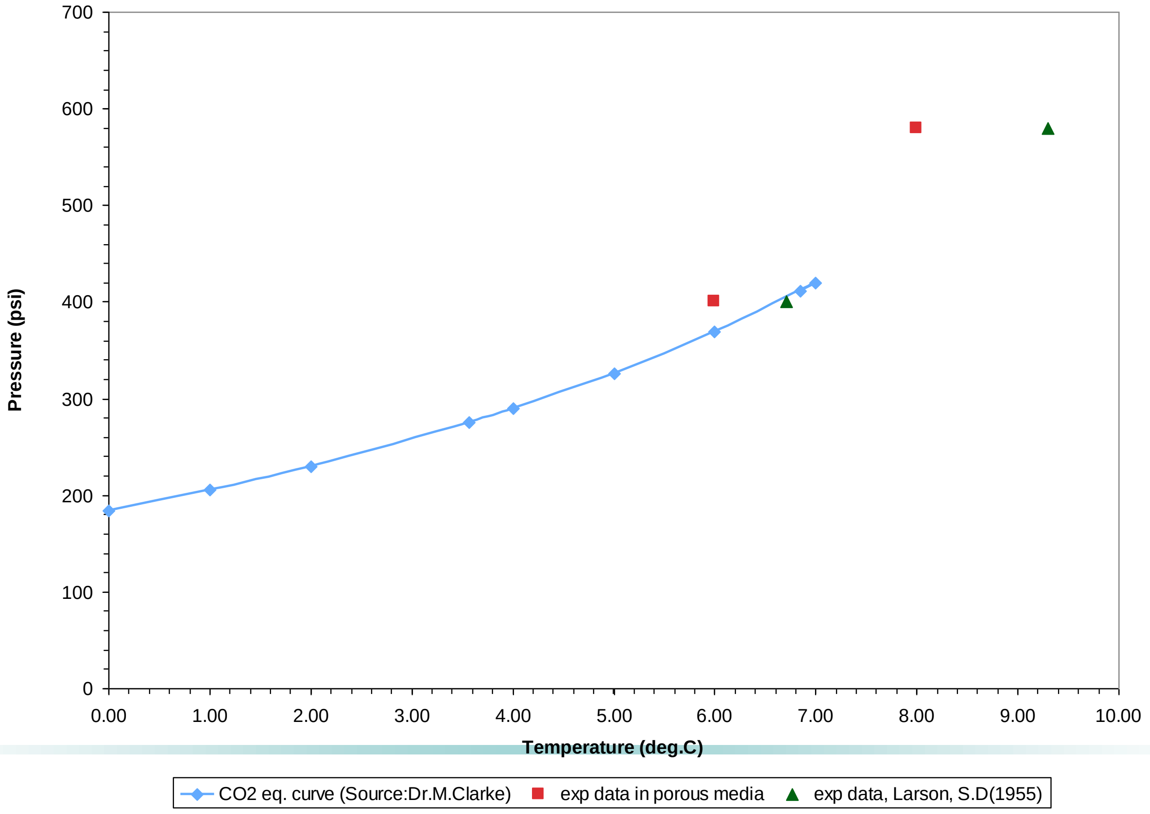
Veins of hydrate

Formation of gas hydrates in porous media.

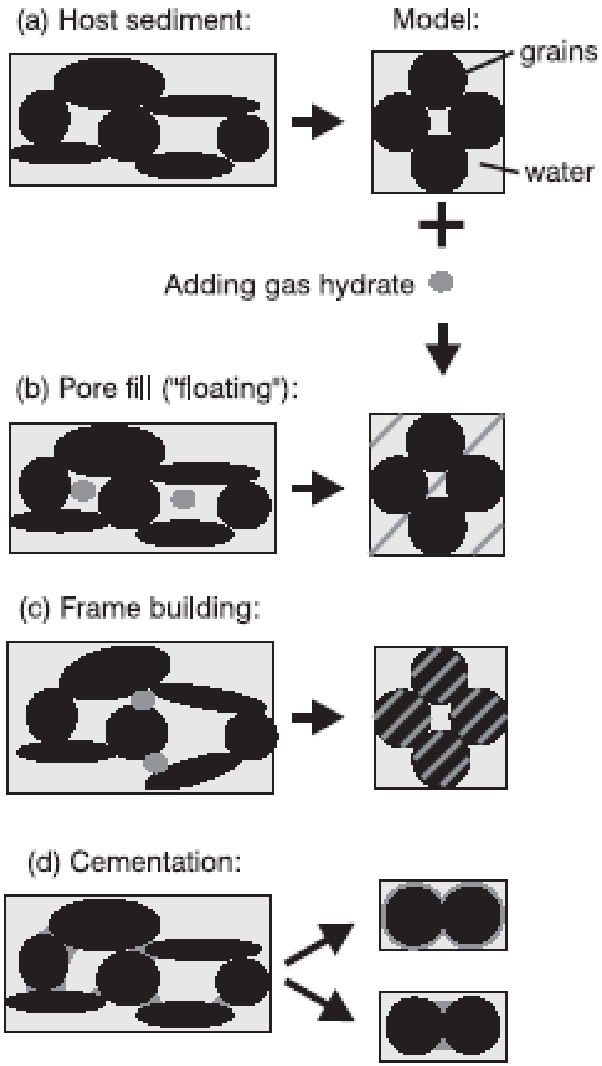
- It has been debated whether hydrates formation is preferentially on grain surface or in the center of the pore space (Kleinberg et al. 2003; Clennell et al. 1999).
- A second important question is the degree to which pore size and surface properties of the host sediment grain influence hydrate growth and distribution.
- Experiments show that porous media modify the stability of clathrate hydrates according to the pore size and surface properties of the host material (Sloan, 1990; Yousif and Sloan, 1991; Handa and Stupin, 1992).

Formation of gas hydrates in porous media.

- The porous medium decreases the stability range of hydrate. A greater pressure or a lower temperature is necessary to form the hydrate.



Distribution of gas hydrates in porous media



Permeability in presence of hydrates.

- One of the very important unknowns in modeling hydrate formation and dissociation in porous media is the permeability variation in the presence of hydrates.
- If the permeability of the hydrate zone is very small, dissociation of hydrate will only occur at the interface between the free gas zone and the hydrate layer.
- If the hydrate zone has some permeability and there exist a mobile fluid phase in the hydrate zone, the pressure reduction will travel to a larger extent in the porous medium thus causing dissociation of hydrate to occur over a larger volume of hydrate.
- In the absence of reliable experimental data, various permeability models have been used in the numerical modeling studies.

Absolute and relative permeability in presence of hydrates.

- Permeability reduction in porous media in the presence of hydrates occurs as a result of the decreasing porosity due to hydrate formation.
- It can also be compounded by plugging of migration pathways.
- If a thin film of hydrate coats the grain walls, changes in the permeability are expected to be small.
- However, the permeability reduction can be more severe if hydrate were to form in the middle of the pore space, with potential to plug pore throats.
- The formation habit of hydrates in pores is poorly understood.
- It is not known whether hydrate tends to form at grain contacts and cement the frame even when its quantities are small or it uniformly coats the grains, so that the cementing effect increases progressively with the hydrate volume.
- Or hydrate tends to form in the center of pores with a partial support to the frame.

Absolute and relative permeability in presence of hydrates.

- Acoustic and seismic data are commonly used in attempts to understand the pore-space growth habit of hydrate (Berge et al. 1999; Helgerud, 2001; Lee and Collett, 2001 etc).
- Lab study suggests that the cementing effect of hydrate on the sand grains occurrs at saturation above 35% (Berge et al. 1999; Helgerud, 2001; Lee and Collett, 2001 etc).
- Analysis of acoustic data from Blake Ridge, Alaska, and the Mackenzie Delta (Helgerud, 2001; Lee and Collett, 2001 etc.) pointed towards the pore-filling behavior.
- Glass micro model studies for CH4 and CO2 hydrates suggest that a thin film of water persists on grain surfaces and hydrate preferentially formed within the center of pore spaces rather than on grain surfaces (Tohidi et al. (2001)).

Empirical permeability correlations

- Based on parallel capillary models:

1. Hydrate coats capillary walls.

$$k(S_h) = k_o(1 - S_h)^2$$

2. Hydrate occupies capillary centers.

$$k(S_h) = k_o\left[1 - S_h^2 - \frac{(1 - S_h)^2}{\log(\frac{1}{S_h^{0.5}})}\right]$$

Empirical permeability correlations

- Based on Kozeny grain models:

1. Hydrate coats the grains.

$$k(S_h) = k_o (1 - S_h)^{n+1}$$

Where, n equals 1.5 for 0 < S_h < 0.8 and diverges for S_h>0.8

2. Hydrate occupies pore centers.

$$k(S_h) \; = k_o \frac{(1 - S_h \;)^{n+2}}{(1 + S_h^{0.5})^2},$$

Where, the saturation exponent $n = 0.7S_h + 0.3$

Empirical permeability correlations

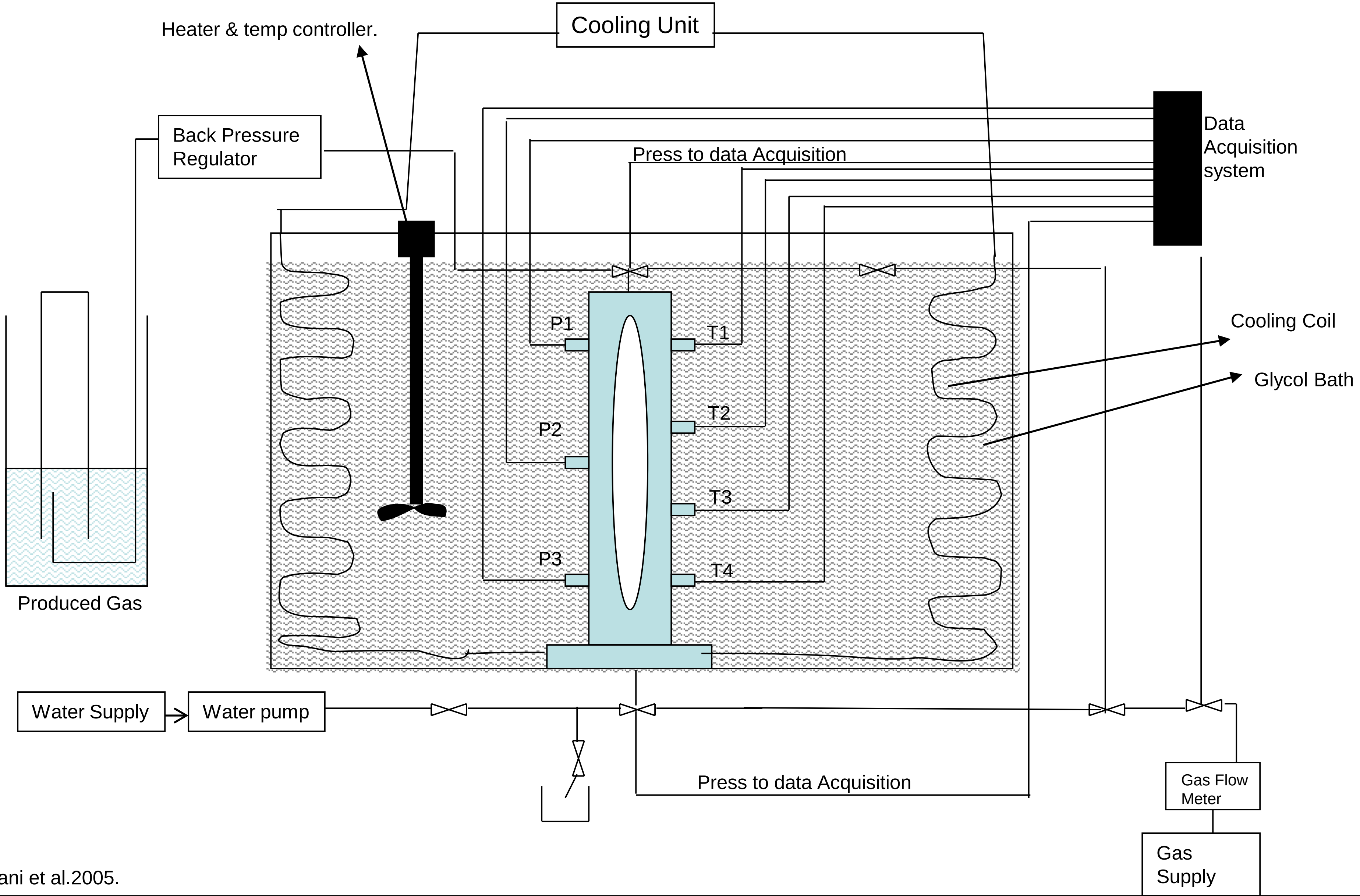
- University of Tokyo model (Masuda et.al. 1997)

$$k(S_h) = k_o(1 - S_h)^N$$

Where, N is the permeability reduction exponent,

which varies from 2 to 15.

Measurement of permeability in presence of hydrate:



Anjani et al.2005.

Comparison of grain coating model and pore filling model:

Hydrate Sat. (S_h), in %	k_{exp}	k_c (Grain coating)	k_f (Pore filling).
20	31.406	38.29007	18.5283
25	26.742	32.58475	14.58664
30	20.054	27.42245	11.40699
35	15.538	22.78477	8.821724
42	7.237	17.13686	5.99432
49	2.576	12.42472	3.904553

- Permeability's are in Darcy's
- for hydrate saturation less than 35%, the experimental values of permeability agree better with its theoretical estimates for the grain coating model.

Ref: Anjani et al.2005

Comparison of Kozeny's equation with Masuda's permeability reduction model:

- Porosity in presence of hydrate is given by:

  $\Phi_t=\Phi_i(1-S_h)$ ….1

- Permeability of a porous media by Kozeny's eq. is given by:

$$K_{initial}=\frac{C_k\Phi_i^3}{({}^{A_s}/_{V_t})^2}$$

…..2

Inserting eq. 1 into 2.

$$K_{abs,sh}=\frac{C_k(1-S_h)^3\Phi_i^3}{({}^{A_s}/_{V_t})^2}=(1-S_h)^3K_{initial}$$

….3

Ref: Anjani et al. 2005

Comparison of Kozeny's equation with Masuda's permeability reduction model:

- Masuda's permeability model in presence of hydrate is given by:

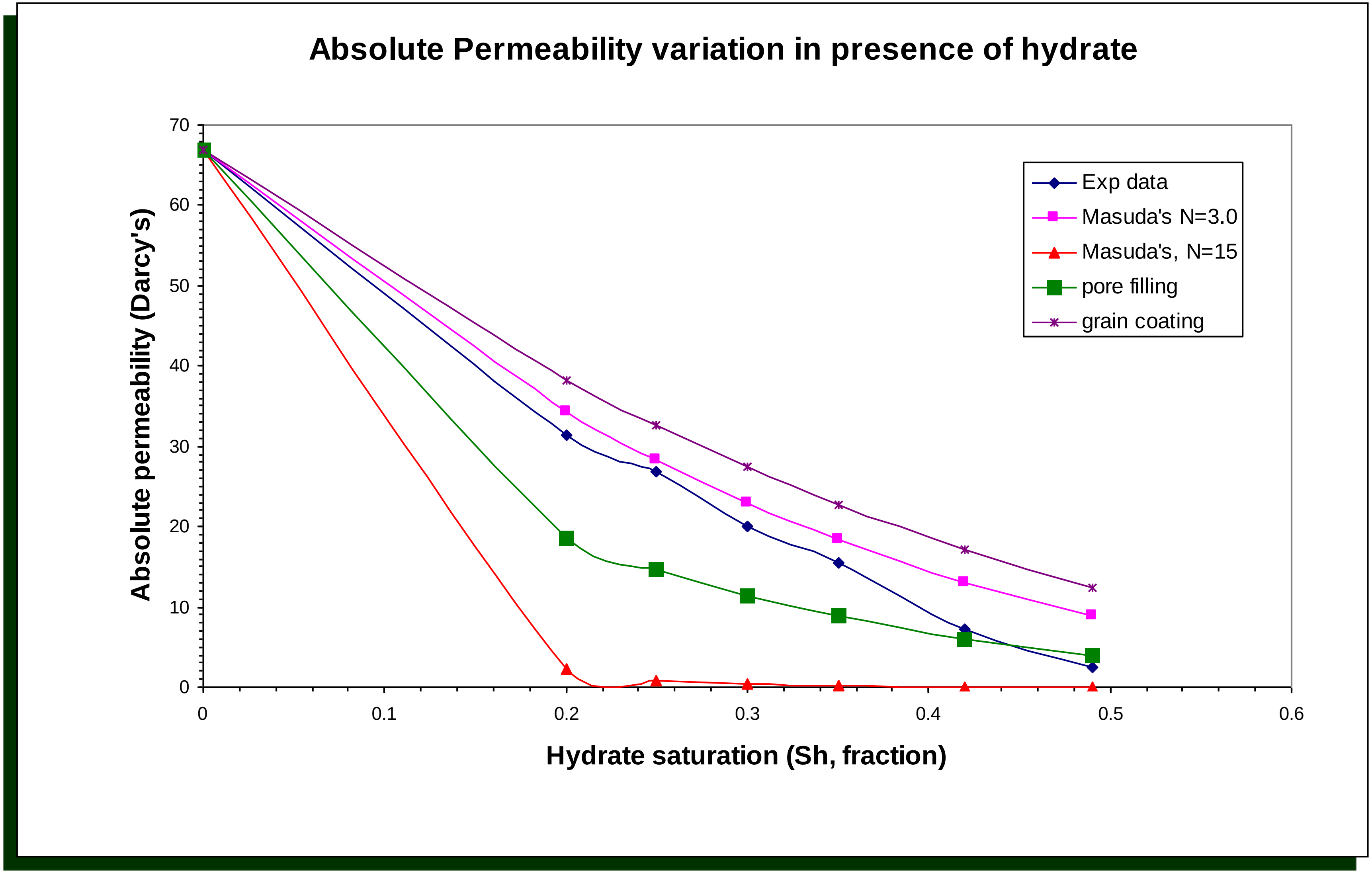
$K=K_0(1-S_h)^N$ ….4

Comparing eq. 3 and 4 we conclude that the value of N should be

~ 3.0

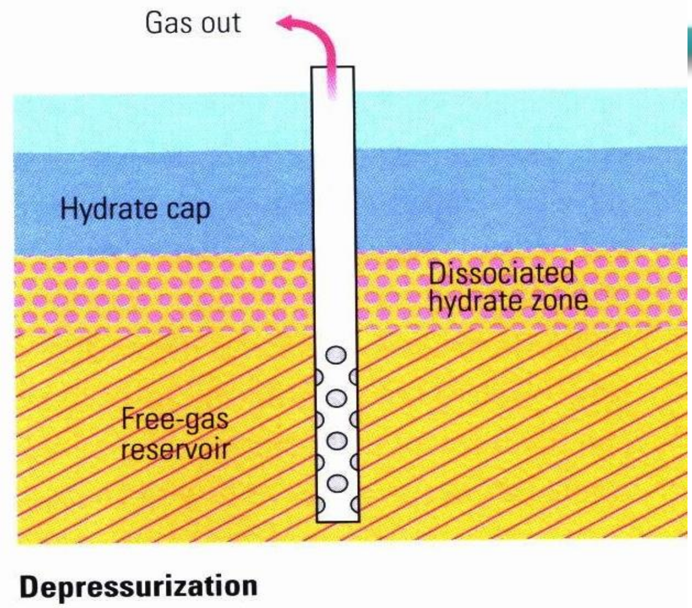
Ref: Anjani et al. 2005

Comparison of permeability models with experimental data:

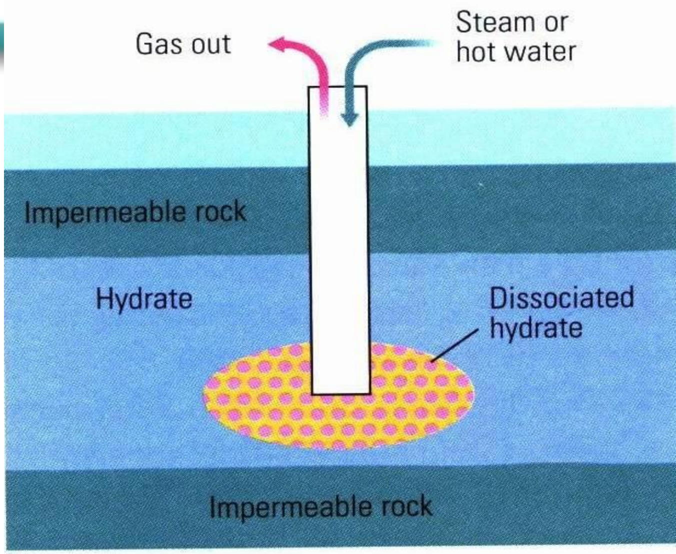


Ref: Anjani et al. 2005

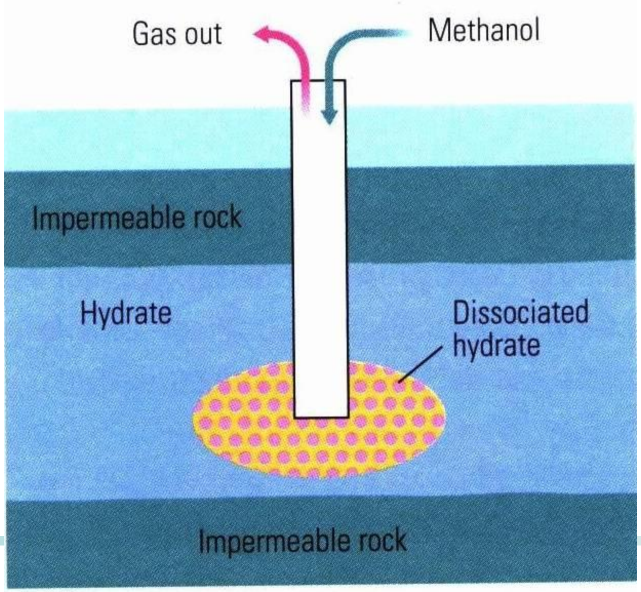
Conceptual Methods of recovery



Depressurization



Thermal Injection



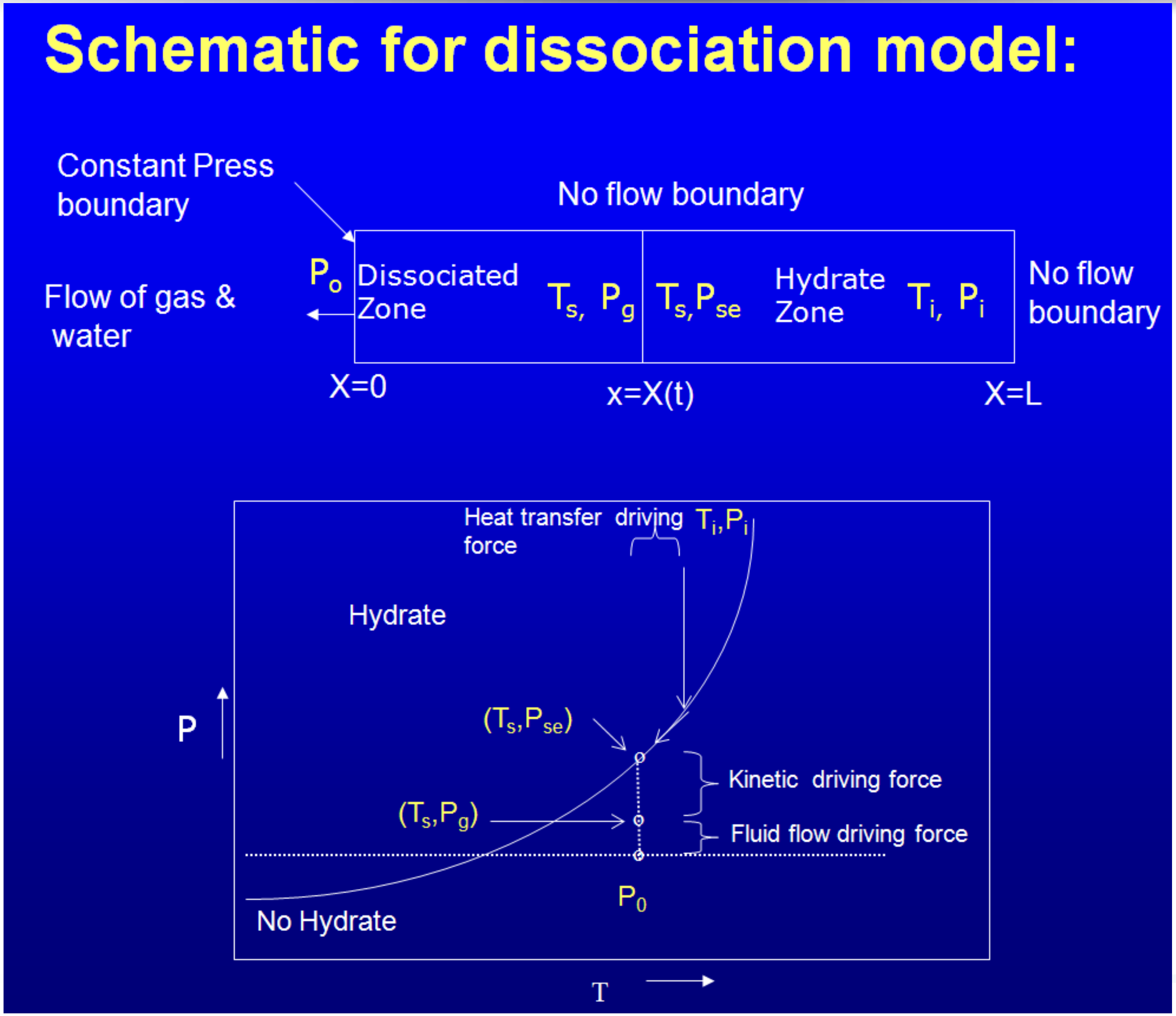
Inhibitor Injection

Dissociation of hydrates :

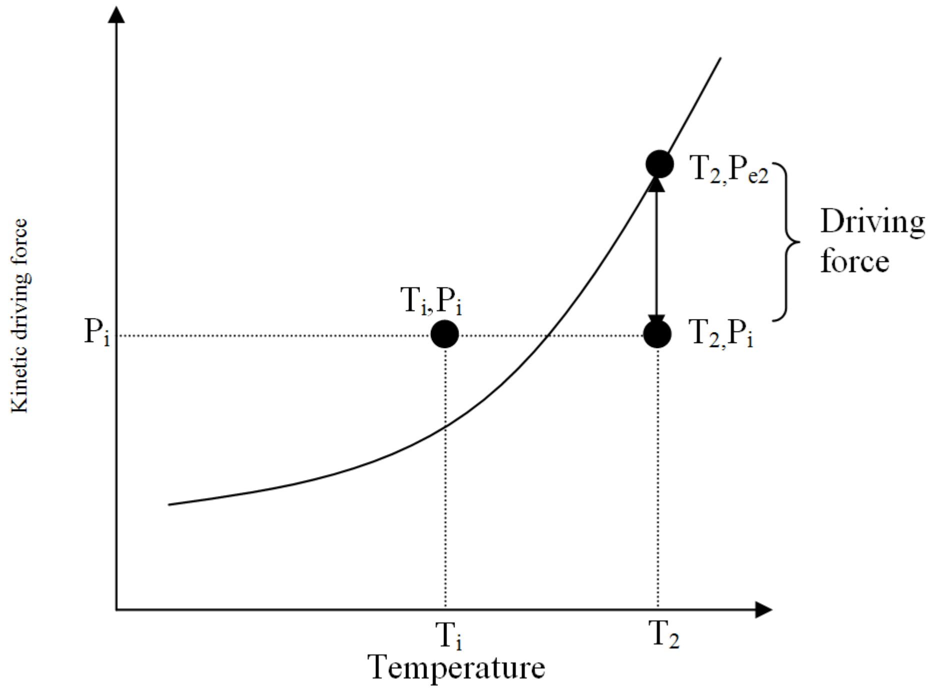
The dissociation process may includes the following mechanisms:

1. Fluid flow through porous media.
2. kinetics of dissociation.
3. Heat transfer through the porous media.

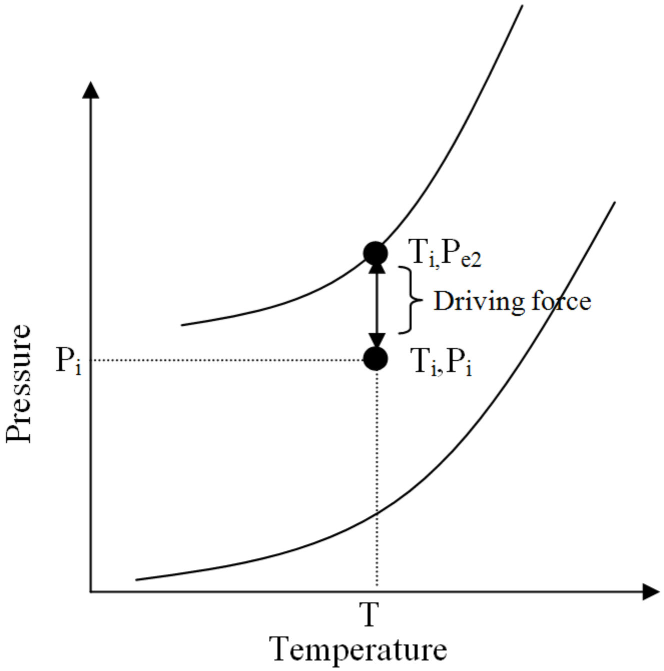
Schematic showing the three driving forces during the dissociation process by depressurization



Schematic for dissociation model:



P-T diagram for thermal stimulation.



P-T diagram for Inhibitor Injection

Kinetics for hydrate dissociation:

❖The basic hydrate dissociation equation is given by:

$CH_4.N_hH_2O$(solid) ↔ CH_4(gas)+N_h H_2O(liquid or ice)

Where N_h is the hydration number.

❖Kim et al. (1987) performed the first quantitative study of gas hydrate decomposition kinetics. They proposed the following equation for the rate of dissociation of gas hydrate:

$$-\frac{dn_h}{dt} = K_{rd} A_{dec} \left(f_e - f_g \right) \ldots\ldots 1$$

The rate of hydrate decomposition is proportional to the surface area of the decomposing particle (A_{dec}), and the driving force of the difference in fugacity of methane at three phase equilibrium condition (f_e) and the fugacity of methane in gas phase (f_g).

Kinetics for hydrate dissociation:

The intrinsic decomposition rate constant, K_{rd}, is the Arrhenius-type temperature dependent coefficient with the activation energy, ΔE, as follows:

$$K_{rd} = K_d^o \exp\left(-\frac{\Delta E}{RT}\right) \ldots\ldots\ldots 2$$

Where, K_d^o is the intrinsic dissociation rate constant of the gas hydrate which is independent of temperature.

Hydrate dissociation surface area:

There are many ways to calculate the hydrate dissociation surface area depending on how the hydrate is distributed in the pore space (coating the surface, present in pore centers etc; This depends on the formation history of hydrate).

One of the methods to calculate the A_{dec} is:

$A_{dec} = \alpha * A_{hs}$

where, α is a shape factor depending on the distribution of hydrate in the pore space.

Method 1:

If hydrate exists at saturation S_h in a porous medium and consists of spherical particles having surface area of A_{hs}, then the effective decomposition area of hydrate per unit volume of the porous medium can be approximated as,

$$A_{dec} = \phi^2 A_{hs} S_w S_h \ldots\ldots 3$$

$$Hence, \alpha = \phi^2 S_w S_h$$

Hydrate dissociation surface area:

- **Method 2:**

  Let Φ_{wg} denote the PV occupied by water and gas per unit volume of porous medium. Using the model given by Amyx et al. (1960), the specific interface area between hydrate layer coating the grain and the fluid phases is given by:

$$A_{dec} = \left(\frac{\phi_{wg}^{3}}{2k} \right)^{0.5} \quad .....4$$

Where, $\Phi_{wg}=\Phi_i(1-S_h)$.

Hydrate modeling in STARS:

- **For dissociation of hydrates the following reaction has to be modelled in STARS.**

$$Rate \text{ of hydrate dissociation} = K_d^o A_{dec}\left(f_e - f_g\right)\exp\left(-\frac{\Delta E}{RT}\right) \ldots..1$$

Where,

K_d^o **= dissociation rate constant.**

f_e **= fugacity of methane at the three phase equilibrium condition.**

f_g **= fugacity of methane in the gas phase.**

A_{dec} **= hydrate dissociation surface area.**

The fugacity can be converted to equivalent pressure considering the coefficient of fugacity to equal to 1.0. This would be an approximation.

Hence,

$$Rate \text{ of hydrate dissociation} = K_d^o A_{dec}\left(P_e - P_g\right)\exp\left(-\frac{\Delta E}{RT}\right) \ldots.2$$

Hydrate modeling in STARS:

$$Rate \text{ of hydrate dissociation } \frac{\mathrm{dc_h}}{\mathrm{dt}} = K_d^o A_{dec} \left(P_e - P_g\right) \exp\left(-\frac{\Delta E}{RT}\right)$$

The above mentioned equation can be easily converted in a format that can be used in STARS

$$\frac{\mathrm{dc_h}}{\mathrm{dt}} = K_d^o A_{dec} P_e \left(1 - \frac{P_g}{P_e}\right) \exp\left(-\frac{\Delta E}{RT}\right) \ldots\ldots 5$$

Where, the ratio of P_e/P_g can be considered as Partial equilibrium K-value. This K-value Can be obtained from the laboratory three-phase equilibrium data ((Pe vs. T).

$$\frac{\mathrm{dc_h}}{\mathrm{dt}} = K_d^o A_{dec} P_e \left(1 - \frac{1}{K}\right) \exp\left(-\frac{\Delta E}{RT}\right) \ldots\ldots 6$$

Hydrate modeling in STARS:

Including equation 3 into equation 6:

$$\frac{\mathrm{dc_h}}{\mathrm{dt}} = K_d^o \phi^2 A_{hs} S_w S_h P_e \left(1 - \frac{1}{K}\right) \exp\left(-\frac{\Delta E}{RT}\right) ......7$$

$$\frac{\mathrm{dc_h}}{\mathrm{dt}} = \left(\frac{K_d^o A_{hs}}{\rho_w \rho_h}\right) (\phi S_w \rho_w)(\phi S_h \rho_h) P_e \left(1 - \frac{1}{K}\right) \exp\left(-\frac{\Delta E}{RT}\right) ......8$$

If we denote the partial pressure in the gas phase as $y_i P_g$, then based on the Raoult's Law, the equilibrium pressure can be defined as,

$$P_e = \frac{y_i P_g}{x_i} ....9$$

Where, y_i and x_i are mole fractions of methane in gas and liquid phase. It is assumed that x_i=1 in the three phase system of liquid water, hydrate and vapor.

Hydrate modeling in STARS:

- Inserting equation 9 into 8 we get the final equation:

$$\frac{\mathrm{dc_h}}{\mathrm{dt}} = \left(\frac{K_d^o A_{hs}}{\rho_w \rho_h}\right)(\phi S_w \rho_w)(\phi S_h \rho_h)(y_i P_g)\left(1-\frac{1}{K}\right)\exp\left(-\frac{\Delta E}{RT}\right) \ldots\ldots 10$$

Another treatment for equilibrium pressure P_e is using the EOS. We can fit the Experimental data into the following form:

$$P_e = a\exp\left(\frac{b}{T-c}\right) \ldots\ldots 11 \text{ where. a, b and c are EOS fitted parameters.}$$

By inserting eq. 11 into eq. 8 we get;

$$\frac{\mathrm{dc_h}}{\mathrm{dt}} = \left(\frac{aK_d^o A_{hs}}{\rho_w \rho_h}\right)(\phi S_w \rho_w)(\phi S_h \rho_h)\left(1-\frac{1}{K}\right)\exp\left(-\frac{\Delta ET - bRT - c\Delta E}{RT(T-c)}\right) \ldots\ldots 12$$

Hydrate modeling in STARS:

- **After simplifying equation 12, we get:**

$$\frac{\mathrm{dc_h}}{\mathrm{dt}} = \left(\frac{aK_d^o A_{hs}}{\rho_w \rho_h}\right)(\phi S_w \rho_w)(\phi S_h \rho_h)\left(1-\frac{1}{K}\right)\exp\left(-\frac{\Delta E_h}{RT}\right) \text{......13}$$

here, $\mathrm{E_h}$ is a new parameter for hydrate activation energy (temperature dependent).

$$\Delta \mathrm{E_h} = \frac{\Delta ET - bRT - c\Delta E}{(T-c)}$$

Stars can handle both eq. 10 and eq.13 (by using the temperature dependent activation energy table).

Hydrate modeling in STARS:

Lets consider equation 10

$$\frac{\mathrm{dc_h}}{\mathrm{dt}} = \left(\frac{K_d^o A_{hs}}{\rho_w \rho_h}\right)(\phi S_w \rho_w)(\phi S_h \rho_h)(y_i P_g)\left(1-\frac{1}{K}\right)\exp\left(-\frac{\Delta E}{RT}\right) \text{......10}$$

term $(\phi S_w \rho_w)$ can be handled by O2CONC keyword (default) presently in STARS.

term $(\phi S_h \rho_h)$ can be handled by the solid phase concentration factor (default).

term $(y_i P_g)$ can be handled by O2PP

term $\left(1-\frac{1}{K}\right)$ should be handled by partial equilibrium reaction (RXEQFOR) keyword.

term 'K' should be generated by the P_e vs T experimental data and rxk1, rxk2..etc should be calculated using some kind of BUILDER interface.

term $\left(\frac{K_d^o A_{hs}}{\rho_w \rho_h}\right)$ = frequency factor in the stars reaction.

Chemical reactions in stars

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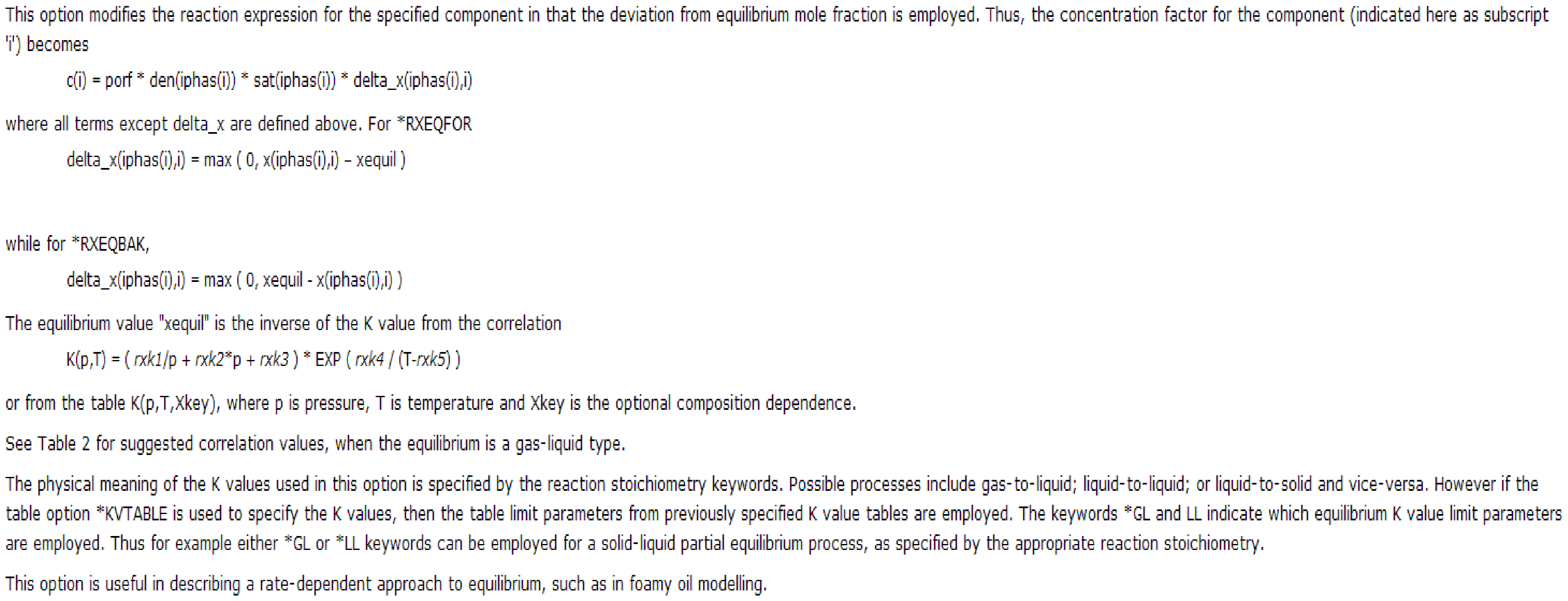
e.g. hydrate dissociation reaction:

```
**COMPNAME 'WATER’   'CH4(g)’   'CH4-HyD'
** Reaction 1: 1 CH4-HyD(s) + 1 WATER ---> 6.75 WATER + 1 CH4(g)
    *STOREAC    1        0        1        **stoichiometric coefficient of reactants
    *STOPROD    6.75     1        0        **stoichiometric coefficient of products
    *FREQFAC      1.097058E+13             **Reaction frequency factor
    *RORDER     1        0        1        **Order of reaction w.r.t. each component
    *RENTH       -51857.9364               ** Reaction Enthalpy
    *EACT       89660.02503                          ** Activation Energy of the reaction.
    *O2PP 'CH4(g)‘   ** partial pressure of gas phase is used for concentration factor.
```

Partial equilibrium reactions in stars

- Used when mass transfer between phases is not assumed to be at instantaneous equilibrium.



This option modifies the reaction expression for the specified component in that the deviation from equilibrium mole fraction is employed. Thus, the concentration factor for the component (indicated here as subscript 'i') becomes

c(i) = porf * den(iphas(i)) * sat(iphas(i)) * delta_x(iphas(i),i)

where all terms except delta_x are defined above. For *RXEQFOR

delta_x(iphas(i),i) = max (0, x(iphas(i),i) – xequil)

while for *RXEQBAK,

delta_x(iphas(i),i) = max (0, xequil - x(iphas(i),i))

The equilibrium value "xequil" is the inverse of the K value from the correlation

K(p,T) = (rxk1/p + rxk2*p + rxk3) * EXP (rxk4 / (T-rxk5))

or from the table K(p,T,Xkey), where p is pressure, T is temperature and Xkey is the optional composition dependence.

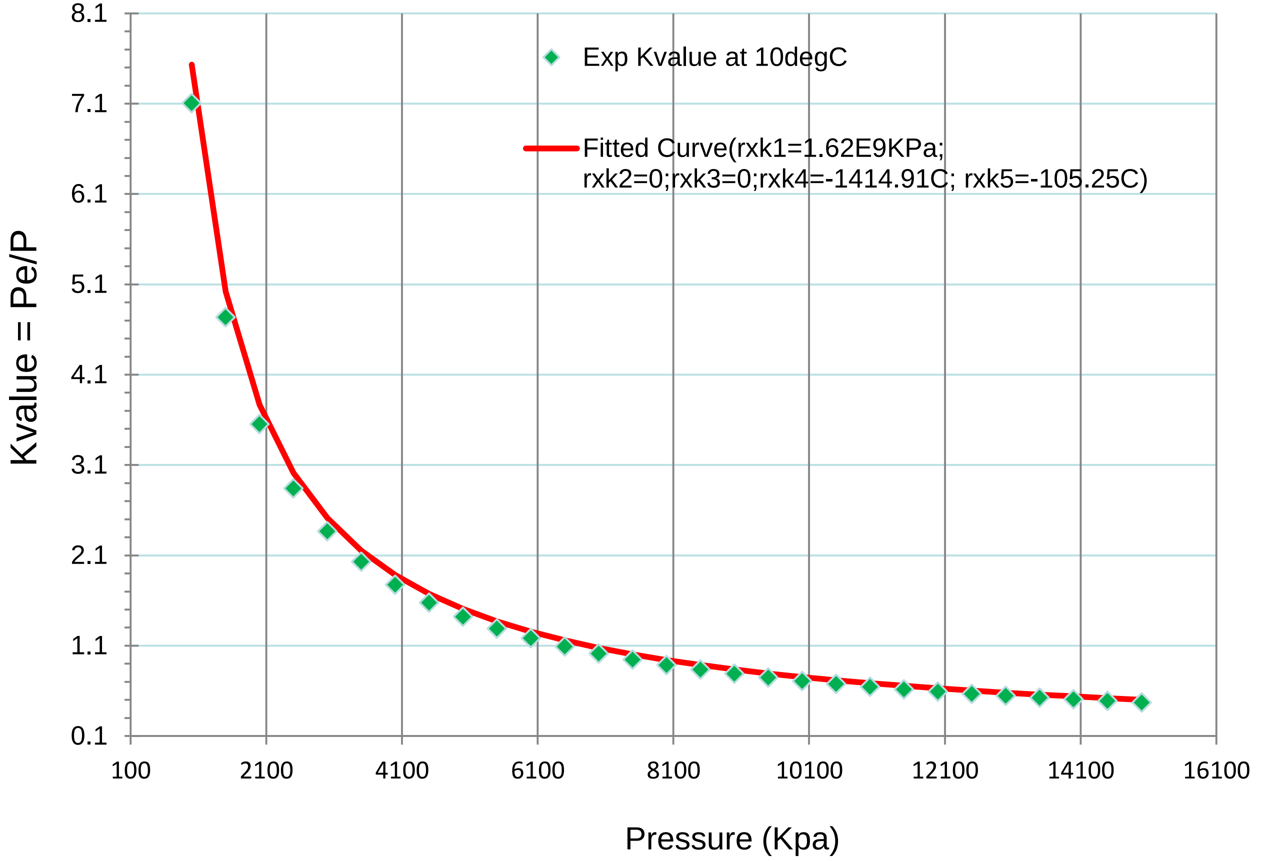
See Table 2 for suggested correlation values, when the equilibrium is a gas-liquid type.

The physical meaning of the K values used in this option is specified by the reaction stoichiometry keywords. Possible processes include gas-to-liquid; liquid-to-liquid; or liquid-to-solid and vice-versa. However if the table option *KVTABLE is used to specify the K values, then the table limit parameters from previously specified K value tables are employed. The keywords *GL and LL indicate which equilibrium K value limit parameters are employed. Thus for example either *GL or *LL keywords can be employed for a solid-liquid partial equilibrium process, as specified by the appropriate reaction stoichiometry.

This option is useful in describing a rate-dependent approach to equilibrium, such as in foamy oil modelling.

Partial equilibrium reactions in stars

- The forward and backward kinetics parameters can be generated either in the form of coefficients or in the form of tables.



Kvalue= ((rxk1/p)+(rxk2*p)+(rxk3))*exp((rxk4)/(T-rxk5))

Hydrate simulation examples

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- Example 1: Hydrate over free gas. Hydrate dissociation by depressurization by producing from the free gas zone.
- Example2: All hydrate zone; Hydrate dissociation by depressurization.
- Example3: All hydrate zone; Hydrate dissociation by hot water cycling.
- Example4: All hydrate zone; illustrates methane hydrate production and Co2 sequestration by co2 hydrate formation.