

NATURAL GAS HYDRATE INHIBITION USING METASTABLE STATES BETWEEN COMPETING CLATHRATE PHASES

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This work summarizes the current understanding of formation and stability of natural gas hydrates - clathrates of methane engaged in crystalline lattice of water - with emphasis on their role as a hazard in natural gas pipelines. A novel method of hydrate formation inhibition is proposed that is based on creation of a metastable state between structure I and II clathrates by changing partial pressures of methane and ethane in natural gas flow. The work encourages future experiments that would look at the range of partial pressures of ethane added to methane gas that would lead to clathrate formation suppression.

Key words: natural gas hydrate, hydrate formation, metastable states, crystallography, flow assurance.

Inhibicija hidrata prirodnog plina uporabom metastabilnih stanja između konkurentskih klatratnih faza. Ovaj rad sažima trenutno razumijevanje formiranja i stabilnosti hidrata prirodnog plina - klatrata metana zatvorenih u kristalnu rešetku vode - s naglaskom na njihovu ulogu kao uzročnika šteta u plinovodima. Nova metoda inhibicije hidrata se temelji na stvaranju metastabilnog stanja između struktura I i II klatrata promjenom parcijalnih pritiska metana i etana u protoku prirodnog plina. Rad potiče buduće pokuse u kojima bi se pratio raspon parcijalnih tlakova etana dodanog metanu koja bi rezultirali suzbijanjem klatratne formacije.

Ključne riječi: hidrat prirodnog plina, tvorba hidrata, metastabilna stanja, kristalografija, osiguranje protoka.

INTRODUCTION

Natural gas hydrate looks like an ice but it does not behave like it. It is a clathrate - a guest-host system formed by natural gas guest molecules and water at high pressure and low temperature. Natural gas hydrates are subject of active research for several reasons. First, methane hydrates present in permafrost regions and at the bottom of oceans have the potential to become a fuel for the future [1]. Second, hydrates can be a suitable medium for cheap, safe and high density industrial storage of methane. Third,

hydrates can play a role in natural gas and CO₂ sequestering [2]. Besides these positive applications, natural gas hydrates also are a hazard to plug-in gas pipelines [3]. Inhibition of their formation in pipeline systems is of very high priority [4, 5].

Presented paper focuses on natural gas hydrate structure and stability applying principles of crystallography and theory of clathrate formation, considering molecular interactions at physical conditions where clathrate formation occurs.

A diagram shown on the right side in Figure 1 describes natural gas hydrate formation mechanism: A guest molecule (methane CH_4 , ethane C_2H_6 , propane C_3H_8 , butane C_4H_{10} , or other molecule with suitable size) is surrounded by host water molecules clustered together by hydrogen bonds. Presence of water molecules at sufficiently high concentration in a liquid or gas environment is critical for forming and stability of gas hydrate [6, 7, 8, 9]. The hydrate stability zone is in high pressure and low temperature region above the pressure-temperature equilibrium curve shown in thin black color on the left bottom side in Figure 1. From the perspective of gas pipeline plugging risk, the region above and to the left of the equilibrium curve is a high risk region, whereas the region below and to the right of the curve is a no risk region. Shifting

the thick blue highlighted pipeline curve to the right by adding heat, or shifting the black highlighted clathrate stability equilibrium curve to the left by adding inhibitors, will prevent hydrate formation.

Note that commonly used gas hydrate inhibitors have negative environmental impact and their costs represent 5% to 8% of gas total costs [10]. A new class of environmentally friendly inhibitors is discussed in [11]. To further reduce cost, new techniques are needed that supplement or replace the use of inhibitors.

This paper includes a proposal to explore a new method of hydrate formation prevention in gas pipelines by creating a metastable state between two clathrate crystalline phases by changing partial pressures of methane and ethane in natural gas flow.

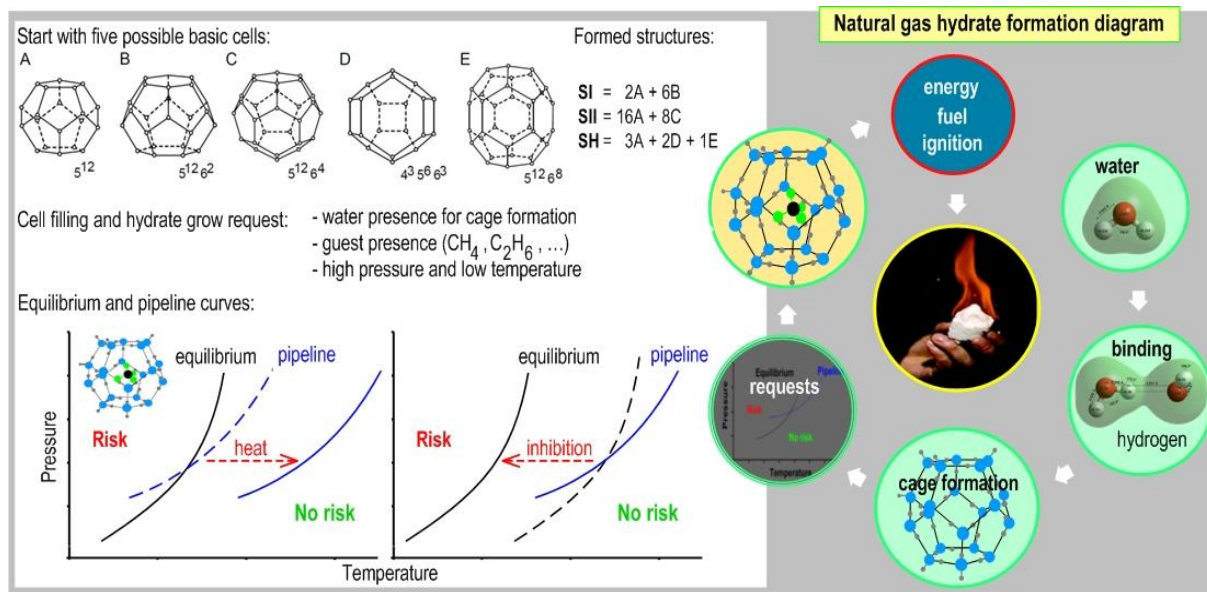


Figure 1. Natural gas hydrate formation cycle is shown on the right. Equilibrium curve divides the pressure-temperature diagram on the left to regions with/without hydrate formation risk.

Heating or addition of inhibitors shift the curves to protect pipelines from hydrate growth

Slika 1. Ciklus hidrata prirodnog plina je prikazan na slici desno. Krivulja ravnoteže dijeli dijagram tlaka i temperature na lijevoj strani u regije sa / bez rizika formacije hidrata. Grijanje ili dodatak inhibitora pomiče krivulje u smjeru zaštite cjevovoda od rasta hidrata

STABILITY OF NATURAL GAS HYDRATE

Clathrate stability depends on molecular bonds between the host molecules forming the cage as well as the nature of guest molecules. Guest molecules influence the stability not only by their size but also by their van der Waals interactions with cage walls. Research on clathrate stability is based not just on quantum chemistry computations but also on experimental results and crystallographic measurements.

It is known that there is a relationship between van der Waals diameter of the guest molecule (i.e., the incidence of van der Waals forces) and the free space in the cage cavity, which defines the structure of the created crystalline lattice [13]. Based on the range of Waals diameters of guest molecules, we recognize two different system types, as also shown in Figure 1:

van der Waals diameter range	possible guests	structure	System type
4.2 to 5.8 Å	CH ₄ and C ₂ H ₆	cubic	SI (system I)
5.8 to 7.0 Å	example: C ₃ H ₈	cubic	SII (system II)

Special group of clathrate hydrates are with Ar, Kr, N₂ and O₂ guests. These atoms or molecules with diameters lower than 4.2 Å form hydrates of the system SII at lowest pressures [14]. It was assumed that Helium and Neon might not be able to form hydrates since their atoms are too small for stabilization of clathrate hydrate cages - and indeed the formation of such clathrates has not been observed yet. However, it was experimentally confirmed that another very small guest - a hydrogen molecule - can form hydrate type SII at the pressure and temperature range: 2 - 3 kBar and 240 - 249 K, respectively [13]. This is possible thanks to filling the host cage with more than one hydrogen molecule. Small cages of hydrate type SII are filled with one or two hydrogen molecules, while bigger cages can be filled

with one to four hydrogen molecules. Such finding together with theoretical calculations is encouragement for those searching for hydrogen or neon hydrates [13].

Clathrates of gas mixtures sometimes form structures that are different from the crystalline structures favorable for individual gas mixture components. For example the gas mixture of methane and ethane forms the structure of type SII while both methane and ethane alone forms the structure of type SI. It is worth mentioning that this behavior is similar to that of some metallic alloys. There is a potential to leverage from the wealth of crystallography and thermodynamics knowledge about alloy structure and phase formation, as the crystalline structures of some alloys show similar configuration to clathrate hydrates.

PROPOSAL FOR HYDRATE FORMATION PREVENTION IN GAS PIPELINES USING METASTABLE STATES

As explained above, the structure of clathrate hydrates is stabilized when the size and composition of guest molecules meets the size and composition of host cages, with two different cage structure types being formed (SI and SII), depending on guest molecule size. To inhibit natural gas hydrate formation in gas pipelines, we propose to set conditions at which there will be "a competition" of free energies of multiple structures. Such multiple phases "competition" can prevent the crystal formation. Specifically, we propose to achieve phase interface between structures SI and SII by change of partial pressures of more-component gases - methane (CH_4) and ethane (C_2H_6) in natural gas.

As described above, clathrates of gas mixtures sometimes form structures that are different from those of their individual components. New predictive techniques are being developed to elucidate if gas mixtures can lead to creation of completely new crystalline structures, different from the known clathrate hydrates, in analogy with the behavior of metal alloys. With the aid of thermodynamic analysis, work [15] studied if a recipe can be found for the formation of new clathrate hydrate cage structures stabilized by the presence of specific guests with high adaptability for such cages. We propose to apply a procedure similar to the

one introduced in work [15] in a new way: to identify conditions for formation of metastable states rather than to identify stable structures. If such metastable state is found, it will act as a crystallization barrier, which is welcome in cases where crystallization is undesired.

The wide range solution of such a task is much complicated since it is not possible to count the influence of all interactions which can appear in such case. The key is in selection of models that will simplify this case without ignoring crucial interactions involved in clathrate formation. One of the models allowing investigation of clathrate stability comes out from the equilibrium of empty hydrates with guest gases where the chemical potential of water is approximated in the following way:

- i) Interactions between guests are neglected;
- ii) Changes of the host cages mediated by guests are neglected;
- iii) Each cage is occupied maximally with one guest molecule.

However, if guest molecule is too big, modulation of vibrational frequencies of the host can occur, so that previously considered host-guest interaction will be ignored.

THERMODYNAMIC SOLUTION

If we accept assumptions from above, the total statistical sum can be written as a product of particular statistical sums of hypothetically empty clathrate hydrates with

N_k k -hedral cages in unit cell and the guests of type j with chemical potential μ_j , as follows:

$$\Xi = \exp(-\beta A_W^0) \prod_k \left[1 + \sum_j \exp(\beta(\mu_j - f_j^k)) \right]^{N_k} \quad (1)$$

In eq.(1) A_W^0 represents the free energy of a hypothetically empty clathrate hydrate; f_j^k is a free energy of guests j in k -hedral cage, where k flows through the possible cage

types and $\beta = \frac{1}{k_B T}$. Free energy of the cage occupancy for a gas with spherical molecule can be expressed by equation (T+K):

$$f = -k_B T \ln \left[\left[\frac{mk_B T}{2\pi\hbar^2} \right]^{3/2} \int_{V_{cage}} \exp(-\beta w(r)) dr \right] \quad (2)$$

Here m and $w(\tau)$ represents the guest molecule mass and guest-lattice interaction, respectively. This interaction is usually expressed by Lennard-Jones potential describing an interaction that is weak attractive at longer distances and becomes highly repulsive when molecules move close to each other. This potential can be expressed by equation:

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right],$$

where σ and ε represents the counted two particle equilibrium distance and the interaction strength, respectively. During calculations, Lennard-Jones interactions are often cut off at the distance 3σ . The dynamic influence of such cut-off is negligible and a speed up of calculation is dramatic. Integration passes through the inner of one cage. Quantity f represents molecular „convenience“ for such a cage. The chemical potential of the guest is approximated by chemical potential of an ideal gas:

$$\mu_j = -k_B T \ln \left(\left(\frac{2\pi m_j k_B T}{h^2} \right)^{3/2} \frac{k_B T}{p_j} \right), \quad (3)$$

where partial pressure can be inserted as an independent variable. The chemical potential of water μ_c can be derived from statistical

sum of a set of N_w water molecules as follows:

$$\mu_c = -k_B T \frac{\partial \ln \Xi}{\partial N_w} = \mu_c^0 + \Delta\mu_c, \quad (4)$$

where μ_c^0 and $\Delta\mu_c$ is chemical potential of a hypothetically empty water cage and cage lattice-guest interaction contribution,

respectively. Quantity $\Delta\mu_c$ can be expressed in a following form:

$$\frac{\Delta\mu_c}{k_B T} = -\frac{\partial \ln \Xi}{\partial N_w} = -\sum_k \alpha_k \ln \left[1 + \sum_j \exp(\beta(\mu_j - f_j^k)) \right] \quad (5)$$

where α_k is the count of k -hedral cages corresponding to one water molecule in one unit cell, so that $\alpha_k = N_k / N_w$.

To evaluate clathrate stability condition, we need to find the minimum of quantity $\Delta\mu_c$. This is a difficult task, due to the existence of significantly discrete distribution of cages. Finding minimum of $\Delta\mu_c$ is different from calculation of minima using methods of mathematic analysis. In our case the dominant role is played by the topography of cages in crystallographic systems. Guest molecule interacts with oxygen atom of water molecule, located on the cage lattice, within a short-distance Lennard-Jones interaction. A dominant contribution comes from the cage, where the guest is situated. Contribution from neighboring cages that are sharing one of the edges with this cage also cannot be neglected.

To solve this complex task, work [15] employed empirical patterns as follows:

- The first is an existence of Frank-Kasper structures. Atoms in densely packed tetrahedral alloys are arranged in these structures. Because cages in hydrates of inert gases behave similarly to these alloys, it was possible to consider (in correspondence with Frank and Kasper) just those hydrate structures whose cages consist of pentagonal and hexagonal faces.

CONCLUSION

Natural gas hydrate formation prevention in gas pipelines is an important issue for gas transport industry. This is typically accomplished by use of inhibitor chemicals, which can have negative environmental impact and adds considerable cost. This work proposes to explore complimentary approach based on exploiting metastable state at the phase interface between structures SI and SII by changing partial pressure of ethane in natural gas. The paper summarizes thermodynamic analysis method from [15] and suggests applying this

- The second empirical rule is Yarmolyuk-Kripyukovich convention that specifies a relationship between the numbers of 12-, 14-, 15-, 16-coordinated atoms in Frank-Kasper structures.

Based on [15], minima of $\Delta\mu_c$ depend on molecular size as follows:

- 1) one of the structures SI, SII, SH yields the lowest value of $\Delta\mu_c$ depending on the type of occupying guests;
- 2) $\Delta\mu_c^0$ for structures SI and SII are lower comparing to $\Delta\mu_c^0$ for structure SH;
- 3) only two structures: SI and SII can be considered as the most stable;
- 4) structure SH is an exception: it can occur at the phase intersection between SI and SII.

We are proposing to use the same framework to uncover:

- Range of partial pressures of ethane in methane to form a metastable state – a phase interface between structures SI and SII
- Search for new types of inhibitors to reduce clathrate stability

analysis in a new way: to identify conditions for formation of metastable states rather than to identify stable structures. This analysis will be carried out in future work and is proposed here to also be a motivation for others.

The work also encourages future experimental work that would look at a range of partial pressures of ethane added to methane gas to uncover feasibility of maintaining such metastable state over practical range of pressure and temperature conditions.

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REFERENCES

- [1] E. D. Sloan Jr.: Fundamental principles and applications of natural gas hydrates. *Nature*. 2003, 426, p. 353-359.
- [2] [26. 08. 2013] K. Wallmann, J. Bialas: Submarine Gas Reservoirs (SUGAR - projekt) <http://www.geomar.de/en/research/fb2/fb2-mg/projects/sugar-i/>
- [3] C. A. Koh, A. Sum, E. D. Sloan, *Natural Gas Hydrates in Flow Assurance*, Gulf Professional Publishing (2010), ISBN 978-1-85617-945-4
- [4] A. Perin, M. O. Musa, J. W. Steed: The chemistry of low dosage clathrate hydrate inhibitors, In: *Chem. Soc. Rev* 2013, 42, p. 1996-2015
- [5] G. K. Folas: Modeling of complex mixtures containing hydrogen bonding molecules, In: *PhD.Thesis*, 2006, Technical University of Denmark
- [6] E. D. Sloan Jr., C.A. Koh: *Clathrate hydrates of natural gases*; CRC Press, Taylor & Francis Group, 2008, p. 690.
- [7] V. Foltin, J. Rajzinger: Natural gas hydrates – challenge and opportunity, In.: 32 *Stretnutie katedier Mechaniky tekutín a Termomechaniky*, Vysoké Tatry -Tatranská Lomnica 2013, Proceeding – Zborník príspevkov, Žilinská Univerzita v Žiline, ISBN 978-80-554-0715-9, p. 45-48.
- [8] [26.8.2013.] V. Foltin, invited lecture in: <http://www.spnz.sk/presentations.html>, Central European Gas Conference (CEGC_Presentations_2013), 5th Panel - The Use of Natural Gas and Unconventional Gas sources V. Foltin, J. Rajzinger STU Bratislava: J. Rajzinger, V. Foltin, F. Ridzon: *Natural Gas Hydrates*.
- [9] V. Foltin, J. Rajzinger, F. Ridzoň: Structural view to natural gas hydrates. In: *The application of experimental and numerical methods in fluid mechanics and energetics 2014 : proceedings of the international conference. Liptovský Ján, Slovakia, 9-11 April, 2014. - Žilina : University of Žilina, 2014. - ISBN 978-80-554-0855-2. - S. 39-44*
- [10] B. Chandragupthan: An insight to inhibitors, In: *PetroMin Pipeliner*. 2011; July-Sept, p. 50-57.
- [11] V. Foltin, J. Rajzinger: Drive towards environmentally friendly inhibitors for natural gas hydrate formation prevention, submitted to: *The holistic approach to environment*

- [12] [26.8.2013]
<http://www1.lsbu.ac.uk/water/index2.html>, M. Chaplin: Water structure and science
- [13] V. Belosludov et al.: Prediction of structure, composition and phase behavior of helium hydrates. Proceedings of the 7th International Conference on Gas Hydrates; Edinburgh, July 17-21, 2011.
- [14] D. W. Davidson, Y. P. Handa, C. I. Ratcliffe, I. S. Tse, B. M. Powel: The ability of small molecules to form clathrate hydrates of structure II, In: Nature. 1984; 311, p. 142-143
- [15] M. Matsumoto, H. Tanaka: On the structure selectivity of clathrate hydrates, In: J. Phys Chem. B 2011, 115, p. 8257-8265