Skoltech
Skolkovo Institute of Science and Technology

Thesis Changes Log

Name of Candidate: Daria Sergeeva

PhD Program: Petroleum Engineering

Title of Thesis: Development of thermodynamic models for phase equilibria of water-ice-gas-hydrate in aqueous solutions of inhibitors and in porous media

Supervisor: Principal Research Scientist Vladimir Istomin

The thesis document includes the following changes in answer to the external review process.

Dear Reviewers,

I would like to express my gratitude for your comments and suggestions to all of you! I found them very useful and implemented them into my thesis. Also, I would consider them in my future research work. Please find the responses to your comments.

Sincerely,
Daria Sergeeva

Reviewer: **Prof. Sergey Stanchits**

Comment 1:
I would recommend Daria to highlight the scientific novelty of preformed studies, for example, in an additional paragraph in the Chapter "Summary of the Research"

Response: Thank you for recommendation, I enhanced the scientific novelty to the introductory section of the thesis.

Comment 2:
I am sure that the possible application of the results of the study to the field conditions is extremely important, and as one of the options, Daria demonstrated applicability of modelling results to prevent hydrate formation in Eastern Siberia. I would recommend to specify: where else in the gas and gas-condensate fields the results of the Ph.D. study could be applied?

Response: Thank you for the positive comment. Other cases where the results of our work can be applied also include Chayadinskoye and Kovykta gas condensate fields, when high-salinity formation water appears in the production wells.

Comment 3:
My additional comment can be considered as a possible recommendation for a further study. I think that modelling of the history of temperature variation over time in the region surrounding new geocryological phenomenon (craters) in Yamal Peninsula could have important practical application, possibly predicting the

moment of the gas bursts that form large-diameter craters.

Response: Thank you for recommendation, I would consider temperature regime modelling as well as dynamics of gas-saturated sediments freezing in my future research work.

Reviewer: **Dr. Vyacheslav Pimenov**

Comment 1:
The difference between gas hydrates forming in a bulk conditions and in pore space could be shown in the thesis more distinctly.

Response: Thank you for this observation. We consider the formation of hydrates in equilibrium with the pore water with modified thermodynamic properties due to its interaction with the mineral substrate. Thus, pore water property (as compared to the bulk water) takes into account in terms of the pore space water activity, which is experimentally measured by using WP4C device. Also, pore space hydrates may be considered as a bulk phase, since the hydrate particles in soils (which are considered in the thesis) have the size more than 10 μm. As for nano-porous media we must take into account the changing of nano-hydrate particles properties (in comparison with bulk hydrate phase).

Reviewer: **Prof. Dimitri Pissarenko**
Comment 1:
Some improvement may be recommended with respect to the English language and style. A final proofreading would spare the manuscript from a few unnecessary typos.

Response: Thank you, we have double-checked the typos manually and also used Grammarly program to correct the grammatical errors.

Reviewer: **Prof. Boris Balakin**

Comment 1:
The novelty of the work is to be explicitly highlighted in the Abstract and the Conclusions.

Response: Thank you, I highlighted the research novelty in the Abstract.

Comment 2:
Table 5.3. It is essential to mention the experimental method used to determine the particle size distribution.

Response: Thank you, to determine the particle size distribution we used two methods: sieve analysis (dry) for sands (particles >0.1 mm), and hydrometer test for clays (in particular, kaolinite).

Comment 3:
An economical estimate that highlights the advantage of mixed inhibitors is to be provided.

Response: Thank you for the comment! Although this is a valid and practical concern, the detailed economic analysis goes beyond the scope of our work.
One particular case study that illustrates the impact of having mixed inhibitors is replacing methanol with the formation water in the Eastern gas–condensate fields of Russia. Formation

water in these fields has a mineralization level of 350 g/l and higher, so we may use the formation water (brine) as hydrate inhibitor as well as the mixed inhibitor “formation water+methanol”. As a result, the operational costs of using formation water or mixed inhibitor “formation water+methanol” may be reduced in comparison with pure methanol.

Comment 4:
"The water droplets with a characteristic radius of 50-100 microns move together with the gas flow", To elaborate on how the drop sizes were determined.

Response: Thank you for your question. We estimated the average size of water droplets in the gas flow using the correlation obtained in the prior work by Guseynov et al. (1977). Also the correlation was published in the monograph by Sinaysky and Lapiga (2002, p. 378), translated to English in 2007. This size depends on the pressure, the temperature, and the velocity of the gas flow, as well as on the surface tension of water.
[1]. Huseynov Ch.S. Determination of the modal size of droplets in a two-phase turbulent flow, 1977, Journal of Applied Chemistry, Issue 4., p. 448-452
[2]. E.G. Sinaiski and E.J. Lapiga, Separation of Multiphase, Multicomponent Systems, 2007, ISBN 978-3-527-40612-8

Comment 5:
It is unclear how Eq.74 is derived. The author to include a detailed description of the conducted thermal analysis.

Response: Thank you, I included the detailed description of the conducted thermal analysis for Eq.7.4 in Appendix 4.

Comment 6:
The thesis is missing: a complete description of limitations of the developed models, a recommendation for further work.

Response: Thank you for providing the feedback. We received similar comments regarding the missing future work directions from other reviewers, and addressed this concern by including them in the conclusions.
As for your comment regarding the limitations of our methodology, they are stated throughout our work in a per-chapter basis. More specifically, chapters 4 and 5 discuss the hydrate and ice particles in porous media that are larger than 10 μm (page 88), and in chapter 6 the limitations for mixed inhibitor correlations are $\triangle T < 25\text{-}30$ (page 123)

Comment 7:
There are typos and grammatical mistakes. Tre commend proofreading the thesis by a native speaker or an Al-based software, f.e. Grammarly.

Response: Thank you, we have double-checked the typos manually and also used Grammarly program to correct the grammatical errors.

Comment 8:
Figures should be in a vector format where possible.

Response: Thank you for the feedback. We do agree with you and we will take the vector format of the figures in our future work.

Comment 9:
The author used the plural "we" in many places of the work, which is supposed to be individual.

To correct.

Response: Thank you for pointing this out. We did make the necessary edits throughout the thesis.

Comment 10:
Figs.2.1-2.3. Does the author develop them? In another case, a reference to be provided

Response: Thank you for pointing this out, reference to Figures 2.1-2.3 have been added to the thesis.

Comment 11:
Fig.7.10 and similar. It is important to distinguish lines by their style rather than colour.

Response: Thank you for recommendation, figures were being corrected.

Reviewer: **Dr. Alexander Shandrygin**
No corrections requested.

Reviewer: **Prof. Bahman Tohidi**
There are 37 points (comments, questions etc.) for the thesis by prof. Tohidi.

Comments 1-5, 7-9 and 20. Many thanks for these comments, where Prof. Tohidi define the main new results, goal and some directions for future development of the thesis.

Comment 1: The new approach for thermodynamic consistency and checking of the experimental data was proposed
Comment 2: The smoothed reference data of the equilibria “gas – ice – hydrate” and “gas – liquid water – hydrate” were obtained
Comment 3: “methanol + magnesium chloride”
Comment 4: The properties of mixed "kinetic + thermodynamic" inhibitors on the examples of “PVP + NaCl” and “PVP + MgCl2” solutions were studied.
Comment 5: A technique for calculating the methanol consumption, which takes into account the formation water producing by the wells and risk of the halite precipitation, has been developed ice/hydrate can be deposited on the internal wall of the pipe.

Comment 6:
It is necessary to develop new thermodynamic models for the description of phase equilibria in gas-saturated soils and sediments, as well as in gas production systems at Northern conditions.

Response: Thank you, it is fixed.

Comment 7: Goal: Further development of thermodynamic models for the description of the phase equilibria of hydrocarbon systems with aqueous phases and gas hydrates in free volume and in porous media (for modeling of geocryological processes and for developing more effective techniques for gas hydrate control during gas recovery).
Comment 8: hydrate deposition on the inner wall of the pipeline in the case of hydrate-free thermodynamic regime of the gas stream at the Yamburg in-field pipelines
Comment 9: The smoothed experimental data of the equilibria “gas – ice – hydrate” and “gas – liquid water – hydrate” are obtained, which allow to provide more accurate thermodynamic calculation of enthalpies, hydrate numbers and the position of the quadruple points.

Comment 10:
Conclusions and recommendations for future work

Response: We received similar comment regarding the missing future work directions from other reviewers, and addressed this concern by including them in the conclusions. So, we include such section into the thesis.

Comment 11:
Platteu or Platteeuw, page 31

Response: Thank you for noting, Platteu was replaced by Platteeuw

Comment 12:
but the assumption about the vacancy of some large cavities is very problematic, especially for hydrate structures II and H, which we believe is the weakest point of the theory). **Commented [TKB1]:** Yes, you are right. Near 100% of large cavities in sII and sH are filled, based on modelling.

Response: Thank you, the text is fixed.

Comment 13:
HydraFLASH [61]. This is software developed at the Heriot-Watt University (Skoltech has an unlimited software license).
Commented [TKB2]: HydraFLASH is a Hydrafact Limited software, which is a Heriot-Watt University spin-out company. Heriot-Watt does not owe the company or the software, but only a shareholder.

Response: Thank you for the remark, it is corrected.

Comment 14:
On the other hand, the advantage of the Istomin-Kwon's program is to obtain the hydrate numbers and degrees of filling of the clathrate cavities of each of the components of the gas mixture.
Commented [TKB3]: HydraFLASH does the same, for point calculations.

Response: Thank you for pointing this out. We did make the necessary edits to the thesis.

Comment 15:
Firstly, we consider the correlation between three phase equilibria with ice and with supercooled water at temperatures below 273 K. Secondly, we develop the technique for checking the thermodynamic consistency of experimental points for three phase equilibria "gas - water (or ice) - hydrate". The proposed approach allows smoothing more correctly the experimental data for different gases and as a result to receive recommended reference data.
Commented [TKB4]: In general smoothing may mask some facts.

Response: Thank you, we agree that the smoothing may mask some facts, for instance, ice premelting and other surface effects.

Comment 16:
The first question is how to smooth out and to describe the experimental data? Pressure dependence on temperature is described usually by the empirical equation:
Commented [TKB5]: English could be improved.

Response: Thank you, it is fixed.

Comment 17:
How the hydrate points in subcooled were measured? Are they Hydrate Dissociation Points?

Response: Yes, these are hydrate dissociation points. Experimental technique is described in the paper (ref 145)

Comment 18:
This method allows identifying areas where experimental data are unreliable and to smooth them.
Commented [TKB6]: How do we make sure? Smoothing can mask some physical facts.
Won't it better to ignore that point which is not in-line?

Response: Yes, we also tested this proposed option (to ignore of some experimental points near 273 K). But it does not give a completely correct result in relation to hydrate number. In principal we agree that the smoothing may mask additional physical effects.

Comment 19:
In Figure 3.6, how do you explain the first point below 0 C, which is not in line with the rest.

Response:
Thank you for pointing this out, you are right, the graph has been corrected (the points on the graph were removed). The lower line is obtained if we extrapolate all experimental data by empirical dependences, it is clearly seen that the lower quadrupole point is below 273.15 K. The upper line presents the smoothening of experimental data in accordance to the proposed scheme. It can be seen that the proposed method gives the quadrupole point close to 273.15 K.

Comment 21:
100 % CO2 (V). Description of Figure 4.3

Response: Thank you, the legend is fixed.

Comment 22:
Figure 4.4 Three-phase equilibrium 'gas – water (ice) – hydrate I' for methane, nitrogen and their mixtures. Curves from I to V correspond to different gas phase compositions: 100 % CH4 (I), 75 % CH4 + 25 % N2 (II), 50 % CH4 + 50 % N2 (III), 25 % CH4 + 75 % N2 (IV), 100 % N2 (V). Dots show four-phase equilibrium 'gas – water – ice – hydrate'
Commented [TKB7]: Are you sure? I think should be Reverse order

Response: Thank you for noting, the legend for figure 4.4 is fixed.

Comment 23:
The first legend in Figure-4.9

Response: Thank you, the description of the Figures 4.9-4.10 has been added.

Comment 24:
Why so many tests on CO2?

Response: Thank you for a question. Also we have similar results for methane, but for CO2 the influence of pressure is more significant.

Comment 25:
da-ta, in figure 5-2

Response: Thank you, it is fixed.

Comment 26:
The different Chapters have slightly different structures, e.g., some do not have a Conclusions. It would be good to have Summary and Conclusion in each Chapter.

Response: Thank you, the conclusions (summary) are presented in all chapters, except the introduction chapter 1 and the review chapter 2. Also general summary of my research is presented at the end of the thesis.

Comment 27:
Page-110, that the electrolyte solutions not only shift of hydrate formation line as thermodynamic inhibitors. Is this limited to electrolyte solutions, not methanol/MEG?

Response: Thank you, the kinetic effect of electrolyte solution is essential. But for thermodynamic inhibitors like methanol/MEG the kinetic effect is rather small.

Comment 28:
To study experimentally the physicochemical properties of mixed inhibitor "methanol + magnesium chloride". Why magnesium chloride?

Response: Thank you, our experimental data of inhibition properties of "methanol + magnesium chloride" solution are practically new. In addition, there are natural deposits of bischofite ($MgCl_2$ on $6H_2O$) in Russia.

Comment 29:
Normally salts are not added to water, due to scale problems. Also solubility KHI in saline water could be a problem. From a practical viewpoint, how salts are added to produced water?

Response: Thank you, salts are not added to the produced formation water.
In the Eastern fields of Russia, formation water (produced with oil) is highly mineralized (brine) and can be directly used as a hydrate inhibitor. For gas production wells, where methanol is used, a mixed inhibitor of hydrate formation (formation brine water + methanol) can be obtained by a natural way. Such case is considered in Chapter 7 for Yarakta field.
In addition, it should be take into account the scale (halite precipitation). To prevent scale, the concentration of the injected methanol may be reduced.

Comment 30:
Let'. Should read Let's.

Response: Thank you, it is corrected.

Comment 31:
Do you think "methanol + magnesium chloride" will be practical application?

Response: Thank you for question, Yes, it is possible, since there are large deposits of bischofite ($MgCl_2$ on $6H_2O$) in Russia (for example, near Volgograd) as well as in Ukraine.

Comment 33:
from -5÷-10 oC up to -15÷-25 oC. Chapter-7, Page 158

Response: Thank you, it is corrected: from -5 up to -25 ^{o}C.

Comment 34:
Suggestions for future work is missing. Please add a section on "suggestions for future work".

Response: Thank you for noting, the section on "suggestions for future work" was added to the theses.

Comment 35:
Some parts look like consultancy work that have converted to Thesis Chapters

Response: Yes, the thesis includes some practical applications from industrial project.

Comment 36:
Some parts seem to be only theoretical with no experimental evidence

Response: Thank you, to my opinion all parts of the thesis (except chapter 3) have both practical and theoretical meaning.

Comment 37:
In one page please write what are you research achievements

Response: Thank you for recommendation, research achievements was added into introduction as a novelty of the research.