

Jury Member Report – Doctor of Philosophy thesis.

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

Name of the Reviewer:

<p>I confirm the absence of any conflict of interest</p>  <p>(Alternatively, Reviewer can formulate a possible conflict)</p>	<p>Date: 08-11-2021</p>
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The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
Good, but I need to ask some questions and I need to read the thesis for the second time.
- The relevance of the topic of dissertation work to its actual content
It seems correlations play a major role, but it not mentioned in the title
- The relevance of the methods used in the dissertation
I need to read the thesis for second time and carefully, but overall it is good.
- The scientific significance of the results obtained and their compliance with the international level and current state of the art

Some new insights has been presented in the thesis.

- The relevance of the obtained results to applications (if applicable)
The thesis presents some case studies, but it was clear whether they have been implemented.
- The quality of publications
Good

The summary of issues to be addressed before/during the thesis defense

Daria Sergeeva, PhD Thesis

DEVELOPMENT OF THERMODYNAMIC MODELS FOR PHASE EQUILIBRIA OF WATER-ICE-GAS-HYDRATE IN AQUEOUS SOLUTIONS OF INHIBITORS AND IN POROUS MEDIA

1. The new approach for thermodynamic consistency and checking of the experimental data was proposed
2. The smoothed reference data of the equilibria "gas – ice – hydrate" and "gas – liquid water – hydrate" were obtained
3. "methanol + magnesium chloride"
4. The properties of mixed "kinetic + thermodynamic" inhibitors on the examples of "PVP + NaCl" and "PVP + MgCl₂" solutions were studied.
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.
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.
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).
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
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.
10. Conclusions and recommendations for future work
11. Platteu or Platteeuw, page 31

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).

BT: Yes, you are right. Near 100% of large cavities in sII and sH are filled, based on modelling.

13. HydraFLASH [61]. This is software developed at the Heriot-Watt University (Skoltech has an unlimited software license).

BT: 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.

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.

BT: HydraFLASH does the same, for point calculations.

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.

BT: In general smoothing may mask some facts and is not recommended

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:

BT: English could be improved.

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

18. This method allows identifying areas where experimental data are unreliable and to smooth them.

BT: How do we make sure? Smoothing can mask some physical facts.

Won't it better to ignore that point which is not in-line?

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

20. Pages 60-63

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

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'

BT: Are you sure? I think should be a Reverse order

23. The first legend in Figure-4.9

24. Why so many tests on CO₂?

25. da-ta, in figure 5-2

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.
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?**
28. To study experimentally the physicochemical properties of mixed inhibitor "methanol + magnesium chloride". **Why magnesium chloride?**
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?
30. Let'. Should read Let's.
31. Do you think "methanol + magnesium chloride" will be practical application?
32. I have many questions for Chapter 6
33. from -5 to -10 oC up to -15 to -25 oC. Chapter-7, Page 158
34. Suggestions for future work is missing. Please add a section on "suggestions for future work".
35. Some parts look like consultancy work that have converted to Thesis Chapters
36. Some parts seem to be only theoretical with no experimental evidence
37. In one page please write what are you research achievements

Provisional Recommendation

I recommend that the candidate should defend the thesis by means of a formal thesis defense

I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report

The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense