
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: Professor Sergey Stanchits

I confirm the absence of any conflict of interest

Date: 02-11-2021

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.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense
The Ph.D. thesis of Daria Sergeeva entitled “Development of thermodynamic models for phase equilibria of water-ice-gas-hydrate in aqueous solutions of inhibitors and in porous media” addresses a very significant issue – modeling of possible mechanisms for the formation and decomposition of hydrates, describing phase equilibria in gas-saturated soils and sediments as well as in inhibitor aqueous solutions. Nowadays, new low-temperature gas and gas condensate fields are being developed in Western Siberia, Russia, and some geological and technological risks accompanying the development may arise from the presence of gas hydrates. Therefore, I consider the topic of Daria’s Ph.D. study interesting, important and potentially applicable to the field studies.

The thesis is well-written, 213 pages long and contains seven chapters, including a detailed literature review, an analysis of thermodynamics of “pore water-gas-ice-hydrates” phase equilibria, a study of physical and chemical properties of mixed inhibitors, which prevent the formation of gas hydrates in pipelines and wells. Based on the analysis of experimental data, two important correlations of inhibitor components have been established, which have a practical application. It should also be noted that the results obtained during the Ph.D. study can be used to optimize the technology of hydrate inhibition with methanol in wellbores and gas-gathering systems.

The content of the dissertation and the implemented methods are entirely consistent with the topic of the Ph.D. study. The results obtained using the state-of-the-art technology are significant.

I have a couple of comments related to the text of the thesis.

- 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”;
- 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?
- My additional comment can be considered as a possible recommendation for a further study. I think that modeling 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.

Overall, despite the above remarks, Ph.D. study definitely represents a significant step forward in modelling of a phase equilibria in gas-saturated soils, sediments and inhibitor solutions. Daria Sergeeva has demonstrated this by participating in two grants from the Russian Science Foundation (RSF) and in three commercial projects. The results of the study were presented at three International conferences and published in more than three papers in the Q1/Q2 ranking journals.

**Provisional Recommendation**

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