

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: Dimitri Pissarenko

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	Date: 19-11-2021
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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

The thesis manuscript presented by Daria Sergeeva entitled “Development of thermodynamic models for phase equilibria of water-ice-gas-hydrate in aqueous solutions of inhibitors and in porous media” consists of seven chapters, including Introduction and Conclusions, and represents a well-structured and complete account of a high quality research work. The problem of hydrate formation is of high relevance for modern gas industry with respect to flow assurance aspect, as well as regarding the risks of methane release from natural hydrates trapped in permafrost formations. An extensive literature review (Chapter 2) of physical, chemical, and thermodynamical properties of hydrate containing multiphase systems provides a solid basis for setting up theoretical foundations for the problems treated in the subsequent chapters. Chapter 3 is dedicated to the analysis of conditions for multiphase equilibria in the presence of hydrates, which is further used for validating the consistency of such equilibria and smoothing of experimental data, including data on specific gases. Chapter 4 treats a similar set of topics in the formulation adapted for porous media, such as hydrate containing soils. This framework is relevant for a number of applied problems involving the presence of natural gas in rocks/soils at low temperatures and formation of gas hydrates in natural conditions. Chapter 5 focuses on the study of the effects of gas pressure on hydrate formation and on behavior of non-

clathrated water in porous media. The outcome of this investigation has a direct impact on the stability conditions as a function of gas pressure, which is a key issue in all attempted technologies of methane recovery from clathrates. Chapter 6 is dedicated to a detailed study of physical and chemical effects of mixed hydrate inhibitors on formation and stability of hydrates. The problem of hydrate formation in gas wells and pipes is a very acute one, and the associated impact on production systems may largely offset the economics of gas recovery, especially in the offshore context. The obtained results enable an extension of known inhibition effects to different gases and their mixtures. They also provide an extrapolation to various PVT conditions, beyond the experimentally studied ones. These results have a significant practical value for the industrial applications related to flow assurance.

The methodology of the research performed during the thesis project is adequate and rigorous, and the manuscript accounts for the motivation, materials, and methods in a systematic way in each chapter. Theoretical frameworks, results of modeling, and laboratory investigations are presented in a clear and well documented style. Overall, the thesis manuscript is structured and written up to the modern international standards. Daria has co-authored eight publications in international and Russian scientific and industrial journals, she also contributed to six conference papers and presentations. The candidate is thus fully compliant with the formal requirements of Skoltech with regard to the number and quality of publications.


I am fully satisfied with the volume and quality of the work performed by Daria Sergeeva in the course of the thesis project, as well as with the overall quality of the presented manuscript.

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.

I confidently recommend the present thesis for the defense.

Kind regards,

Dimitri Pissarenko

A handwritten signature in blue ink that reads "Pissarenko". The signature is written in a cursive, slightly slanted style.

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