

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Valentina Ekimova

PhD Program: Petroleum Engineering

Title of Thesis: Experimental modeling of gas hydrates interaction with a salt solution in permafrost

Supervisor: Dr. Evgeny Chuvilin

Name of the Reviewer: Leading Scientist Dr. Andrey Stoporev

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	Date: 19.09.2022
--	-------------------------

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

Valentina Ekimova presented her doctoral dissertation at a good level of English. There are only minor typos. The dissertation consists of nine chapters, including Introduction and Conclusion ones. The former shows the importance of the issue under consideration while the latter summarizes the study results. The core part of the work reveals the research topic in detail and delivers the experimental and modeling data. The seven chapters (2 to 8) are in a logical sequence and together represent the whole completed study.

The dissertation work is devoted to studying the features of the gas hydrates' interaction with a salt solution in the pore space of hydrate-bearing sediments under various thermobaric conditions. A general review of the work allows one to note a considerable amount of experimental data and a competent interpretation of the research results. This is an undoubted advantage of the work. Separately, I would like to note the author's systematic approach to studying processes that occurred. For example, the number of repetitions of measurements and the preparation of twin samples for the parallel study of the properties of the samples indeed allow reliable data to be obtained. A wide range of physicochemical methods made it possible to link the salts' concentration along the samples' height with the content of methane hydrate and ice in them. A rigorous analysis of the obtained dependencies was carried out. Phenomenological models of "dehydrating" the sediments in the presence of salt migration are proposed. From a practical point of view, the results obtained will help predict and prevent possible hydrate-based hazards during the processing of the Arctic oil and gas fields. It will also make it possible to consider salt migration when designing hydrate-based gas storage.

Nevertheless, I have disclosed several inaccuracies during the reading of the dissertation. There are also some questions.

- 1) The introduction lacks justification for choosing methane hydrate as the object of study. It is helpful to list the typical compositions of biochemical, deep (catagen), and coal gases, with the type of hydrate structure being formed (usually SI or SII). Methane forms the SI hydrate under the conditions under consideration.
- 2) The Novelty indicates that a method has been developed for determining the content of salt ions (Na⁺) in the sand based on measuring the activity of pore moisture. It is not clear how the counterion type will affect the measurements at high concentrations.
- 3) Novelty says "For the first time" in one paragraph. Obviously, everything that is brought out in Novelty must be done for the first time, so this expression is redundant and confusing.
- 4) Fig. 6 is too schematic and lacks two lines of three-phase equilibrium (water-gas-ice and water-ice-hydrate). Also, the quadrupole point is not shown (it is not strictly at 0°C), and the phase fields are incorrectly indicated. Please correct these issues.
- 5) Page 41. There is an error in the enthalpy of dissociation of the hydrate, and it is an order of magnitude higher. 54.2 kJ/mol corresponds to the enthalpy of methane hydrate decomposition into gas and water at 0°C and 0.1 MPa, while this value is 18.1 kJ/mol when decomposed into gas and ice.
- 6) Figure 14. The presented process is solvation rather than a chemical reaction.
- 7) The top right field includes **saturated** solution and NaCl (Figure 15). Please correct this.
- 8) The calculation does not consider the change in brine density during ice melting and hydrate decomposition. How much will this affect the calculation results?
- 9) How was pressure created in the non-hydrate sample in the area of hydrate stability when studying the influence of hydrate presence on salt migration in frozen sediments? If by methane, was the formation of a hydrate observed? It would be more logical to use a non-hydrate-forming gas (under these conditions, for example, it can be nitrogen).

- 10) Calculating the maximum spread of the brine through the sediment volume would be helpful, and it seems likely to be limited by capillary pressure.
- 11) When comparing the effect of a salt solution of various chemical compositions, please indicate in what percentage the concentration of salts is given (wt, mol)
- 12) Also, as a remark, I will note the misnomer and inappropriate expressions encountered in the abstract, for example, activity of hydrate dissociation, porous gas hydrates, reducing negative temperature

In summary, the PhD thesis is a complete scientific qualification work, which solves actual scientific and practical issues. It can be defended as a PhD Candidate qualification dissertation if suggested minor modifications and improvements are addressed or rebutted.

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