Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Maksim Zhmaev

PhD Program: Petroleum Engineering

Title of Thesis: Experimental evaluation of filtration properties of cryolithozone rocks under conditions of formation and decomposition of gas hydrates

Supervisor: Dr. Evgeny Chuvilin

Name of the Reviewer:

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 19-11-2024**

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

Maksim Zhmaev's doctoral thesis, titled "Experimental evaluation of filtration properties of cryolithozone rocks under conditions of formation and decomposition of gas hydrates," is well-structured and demonstrates a commendable level of scholarship, with only minor typographical errors noted. The dissertation consists of seven chapters, including an Introduction and a Conclusion. The Introduction emphasizes the significance of the research topic and defines the purpose and objectives of the study. Chapters 2 and 3 provide a comprehensive analytical review of existing work in the field and suggest promising research directions. The core part of the thesis, Chapters 4 through 6, delves into the research topic in detail, outlining the experimental methods and approaches employed, as well as presenting experimental modeling of the gas filtration through ice- and hydrate-bearing rocks. Chapters 2 through 6 are organized logically, collectively forming a thorough study of the subject.

The dissertation investigates the patterns of gas permeability in sandy and sandy-clay sediments that contain ice and gas hydrates. A thorough review of the work reveals significant labor-intensive and time-consuming experimental runs and a well-structured interpretation of the research findings. The author's systematic approach to studying the processes involved is commendable. The study examines factors influencing gas permeability, including pressure, temperature, sediment type and composition, moisture content, and the type of gas injected. Additionally, it looks at the rate of hydrate decomposition and methane displacement from the hydrate. A wide range of physicochemical methods was utilized, and a rigorous analysis of the resulting dependencies was performed. The dissertation proposes conceptual models of gas filtration during hydrate decomposition and replacing methane in the hydrate with carbon dioxide, considering the effect of hydrate self-preservation. From a practical perspective, the findings will be valuable for the development of gas production technology from hydrates, as well as for forecasting potential complications in the processing of Arctic oil and gas fields within the gas hydrate stability zone.

There were several questions along with some inaccuracies during the dissertation reading I have pointed out below.

1) The abstract modestly mentions that "Changes in the thermobaric conditions of gas- and hydrate-saturated rock strata ... can lead to gas permeation through frozen rock horizons, active gas filtration through talic zones, and gas emissions into the atmosphere. This may include the formation of craters on land and pockmarks on the Arctic sea shelf." Since natural gas hydrates primarily consist of methane, it's important to emphasize the broader consequences of the destabilization of hydrate-bearing rocks. This process can result in a significant loss of energy resources, as a considerable amount of gas is stored in hydrate form. It also leads to the release of large quantities of greenhouse gases into the atmosphere. Thirdly, the destabilization of hydrates can cause rock failures and potentially damage infrastructure facilities located near the emissions source.
2) To ensure clarity and practical relevance in the work objectives, it is essential to specify which natural and industrial processes are being modeled for each type of experiment. This includes the extraction of methane from hydrate, the hazardous decomposition of hydrates under changing thermobaric conditions of hydrate-containing rocks etc.
3) The term negative temperature has a distinct thermodynamic meaning, to which no part of the above paper applies. If you are working with temperatures expressed as negative numbers on non-thermodynamic Celsius, you would rather use expressions like "temperatures below the ice melting point" or "under the ice stability conditions." The terminology "temperatures below 0°C" is not always correct since the melting point of ice depends on pressure and gas composition.
4) How do the model samples used in this study compare to real cores? The results obtained from bulk models and samples subjected to axial loading in a core holder, which aims to approximate their permeability to natural ones, can differ significantly. Additionally, composite core models are often

utilized to achieve the desired filtration properties. Is it possible to scale your results and use them for production tests interpretation?

5) Was the moisture distribution in the sample analyzed before and after the filtration experiment? Micro X-ray computed Tomography would be informative here. Was any moisture loss observed during gas filtration? How was this accounted for in the calculations? Was the error in determining various experimental parameters assessed?
6) It is unclear whether the hydrate was completely decomposed during the experiment with the self-preservation effect. In other words, did the constant value of gas permeability achieved correspond to that of the initial sample without hydrate?
7) All figure captions must indicate the conditions under which tests were conducted, if applicable.
8) In Fig. 17, you seem to confuse the gas-water interface with hydrate-water saturated with gas.
9) Figure 21 includes an unnamed blue line. It seems to be the water-ice equilibrium vs. pressure. Please correct.
10) In the experimental part, it is necessary to justify the choice of different pressures (3 and 4 MPa) for a substitute gas (CO_2 or its mixture with nitrogen).
11) A system with hydrate-bearing rocks is often self-regulating. Indeed, some increase in temperature (usually small) can lead to the decomposition of part of the hydrate and some increase in pressure to the hydrate stability boundary at a new temperature value.
    For reader-friendliness, when discussing the possibility of forming gas accumulation with elevated pressure when the conditions of rock occurrence change, please explain the formation mechanism of such gas accumulations in a hydrate-containing rock.
12) What is the mechanism of accelerated decomposition of preserved methane hydrate when nitrogen is supplied? The setup diagram in Figure 19 indicates that the temperature sensor is installed only at the end of the cell on the gas outlet side. This experimental design does not allow you to assess the uniformity of the temperature distribution within the sample, particularly in the gas inlet region during the gas substitution mode at temperatures slightly below 0°C. This is significant because these conditions are near the stability limit of ice. Consequently, the data you provide on the phase composition of the sample is only indirect. Was there an evaluation of the local increase in the sample's temperature that could trigger the melting of the protective ice crust and stimulate hydrate decomposition?
13) Please clarify the conditions under which the experiments were conducted. When you mention that gas permeability was studied under equilibrium conditions, does that mean the tests were performed solely within the hydrate stability region, and not on the three-phase equilibrium line of hydrate-ice-gas?
14) This work did not track structural transformations (only phase transitions, like ice to hydrate), so it is necessary to correct the last bullet point in section 1.4. Novelty.
15) Comment on the uniformity of hydrate distribution throughout the sample at all stages of the experiment. Can hydrate form/decompose only in the gas inlet/outlet parts of the cell and clog the pores only locally?
16) In the conclusions, it would be helpful to discuss the practical significance of the results obtained and the future direction of this research. Additionally, it would be beneficial to include recommendations for gas production methods from hydrate-bearing rocks. Is the injection of a thermodynamic ice and hydrate inhibitor a promising approach to enhance the rate of hydrate decomposition and improve gas permeability?

In summary, a PhD thesis is a comprehensive scientific qualification work that addresses significant scientific and practical issues. It can be defended as a PhD Candidate qualification dissertation if the suggested amendments and improvements are adequately 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*