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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Anastasia Ivanova

PhD Program: Petroleum Engineering

Title of Thesis: Dynamic modelling and experimental evaluation of nanoparticle application in surfactant enhanced oil recovery

Supervisor: Alexey Cheremisin, Ahmed Barifcani, Stefan Iglauer, Chi Phan

Name of the Reviewer: Prof. Alexei Buchachenko

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:**  **Date: 10-11-2020**

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 Thesis submitted by Anastasia Ivanova to fulfill the requirements of the Skoltech PhD degree in Petroleum Engineering addresses important and scientifically complex problem of enhancing oil recovery from carbonate reservoirs by means of water flooding. The thesis explores the promising way of surfactant and nanoparticle additions to ejected water. It is well understood that the efficiency of this approach intricately depends on many factors characterizing the reservoir, chemical composition of the carbonate rock, its morphology and interaction with oil, especially with the heavy fractions. Most of these factors correspond to the interfaces. Solid-liquid interfacial phenomena determines the rock-oil and rock-water interactions and the possibility to overcome the former by enforcing the latter. Liquid-liquid water-oil interface is no less important for oil recovery from a network of pores typical to carbonate formations. For water flooding, related interfacial phenomena are primarily determined by reservoir temperature and pressure, wettability of rock surface and amount of soluble salts in it. Effects of surfactant and nanoparticle additives are controlled by the same factors and thus may not be always positive. Despite active research, there are still big gaps in available information, needs in advanced methods to characterize carbonate reservoirs and lack of general understanding of the complex phenomena that govern oil recovery, not to mention physico-chemical mechanisms behind them. On this background, the thesis by Anastasia Ivanova provides a significant research impact.

The research presented in the thesis consists of three parts. The first part is devoted to the study of wettability of a carbonate formation using the original oil-saturated samples. The second part includes experimental studies of interfacial tension (IFT) for model water/n-decane system in the presence of surfactants, salts and nanoparticles. Third part presents a complementary modeling within the molecular dynamics (MD) framework. The motivation of focusing on these three particular research directions is nicely exposed in the Introductory Chapter of the thesis with the solid references to the existing state-of-the-art and level of understanding. Despite the complexity of the overall problem setting and its multi-parametric nature, the prime importance of these particular topics is out of question.

Wettability study of the carbonate rocks described in Chapter 2 is based on the novel microscopic approach. It is recognized that wettability, mostly determined by the contact angle measurement, is a local property of the surface. As such, mean rock wettability provides only very rough reservoir qualification. The idea of the thesis is to perform the contact angle measurements at the microscale using scanning electron microscopy imaging. Proper protocols for tracing out the droplet condensation and for contact angle determination from the droplet image were used to probe various areas of the rock surface in the distinct samples. While all original samples were found to be oil-wet, mild and strong extraction of organic components reveals the heterogeneity of the sample surface with the coexisting hydrophilic and hydrophobic domains. The fact that the latter do not disappear even after strong extraction stimulated the author to investigate the structure of the surface by means of the energy-dispersive X-ray and electron energy loss spectroscopy with the fast cryogenic ion beam surface modification. In short, the author proved a common view that the hydrophobic domains are formed by asphaltenes or fatty acids and provided strong arguments that chemisorption involves ionic

bonds between carboxylic groups and Ca cations from the rock. To my opinion, this part presents the main methodological outcome of the thesis, namely, the way to determine wettability at microscale and importance of the ratio of hydrophilic and hydrophobic surface areas rather than of poorly defined mean wettability.

The second part, the studies of IFT of the model water/n-decane system in presence of surfactant and other additives, is more routine by methodology (Chapter 3). What makes it bright is the systematics. The author takes only two surfactants, anionic SOS and cationic EHAC, but conducts the systematic study of IFT depending on their concentration, temperature, salinity and addition of nanoparticles. Conclusions obtained clearly summarized in the Summary to Chapter 3 need not to be repeated here. Important is the fact that they can really guide the search for optimal composition of the additives enhancing oil recovery from a given reservoir.

Chapters 4-6 describe the third research direction – MD modeling of the water/n-decane interfaces in the presence of surfactant, salt and nanoparticles. This part seeks for the most fundamental conclusions in the thesis work. Indeed, the use of adequate MD models and protocols, clever choice of the cationic surfactants with different structures of the hydrophilic heads (prone to hydrogen bond formation with water or not, CTAC and EHAC) allowed the author not only to obtain realistic IFT dependences, but also derive a number of interesting conclusions and physico-chemical interpretations. Some simulations on the anionic SOS surfactant in presence of nanoparticle are also reported. Once again, the systematic approach makes the conclusions practically useful for composing efficient liquids for oil extraction.

Overall, the thesis summarizes the novel and solid research motivated by clearly stated practical goals. Its results cover methodological, practical and fundamental aspects of the problem and promise high impact on the field. Excellent publications in the multidisciplinary and topical journals indicate that the work withstood very serious professional expertise. Yet, the publications enlisted do not cover the whole thesis material, so more are expected to come at least on the MD simulations. Though the thesis does not expose the personal contribution of Anastasia Ivanova explicitly, it is clear that the research presented required from her quite diverse research skills and extremely hard work. Based on this, I have a strong opinion that the thesis submitted should be brought to the public defense.

Nothing is ideal under the moonlight and one can notice quite a few missing pieces, presentation inaccuracies and misprints. None of them is crucial, but I would like to comment a few.

1. Discussing unusual non-monotonic dependence of IFT on temperature, the author always refers to Gibbs theory that predicts the IFT decline at temperature elevation. However, non-monotonic temperature dependence is well known for binary systems (perhaps for water/n-decane as well, I did not search literature in depth). It was explained long ago [see, e.g., J. Phys. Chem. 56, 480 (1952), J. Phys. Chem. A 92, 4023 (1988) and many other works] by the temperature dependence of miscibility. While this explanation may not be precisely applicable in the presence of a surfactant, interpretations provided by the authors (hydrogen bond rapture, surfactant orientation and deeper penetration in one phase or another) have something in

common with the miscibility. It would be interesting and instructive to make at least qualitative alignment of two behaviors.

2. Unexpectedly, the direct comparison between IFT measurements and simulations is rather limited. Aside of the data on the binary water/n-decane system that appear (surprisingly) at the very end in Table 10, only Fig. 33 allows one to comprehend the accuracy of MD simulations in case of EHAC surfactant. It is despite Chapter 3 reports much more extensive IFT measurements with EHAC and SOS, including salinity and nanoparticle effects, while Chapter 4 contains section 2.2, which tells on some other measurements. Although the MD models and protocols used in the thesis warranty qualitatively correct predictions, quantitative comparisons are important for assessing the prospects of MD modelling and the possibilities of its improvement.

As the minor comment, I would indicate useless repetitions on MD formulation at the beginning of Chapters 5 and 6.

Still, I do not consider these and other minor drawbacks as significant and affecting my high assessment of the thesis research and its author.

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*