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Thesis Changes Log

Name of Candidate: Tagir Karamov

PhD Program: Petroleum Engineering

Title of Thesis: Void space evolution and organic matter transformation of Bazhenov Formation rocks during high temperature treatment

Supervisor: Prof. Mikhail Spasennykh

The thesis document includes the following changes in answer to the external review process.

Dear Jury Members,

I am grateful for your comments and suggestions, which help me to improve the quality of the thesis. Here I provide the answers to questions and suggestions. Please find the following changes in the final thesis file.

Reviewer: Professor Dmitry Koroteev

1) *Microscopic issue. When characterizing segmented 3D and 2D images, is it possible to consider topological characteristics responsible for connectivity (percolation thresholds or others) characterization and directional anisotropy of the voids (pores, fracs)?*

Porous media topological characteristics, strictly speaking, should be considered only for 3D cases [1]. Despite the existence of techniques for 3D volume reconstruction from 2D sections using statistical methods (e.g. Gaussian random field) [2], there are no direct stereological methods to achieve 3D topological characteristics from two-dimensional sections [1], especially for anisotropic materials such as shales. However, technically consideration of some topological characteristics in two-dimensional images is possible, particularly percolation theory implies using a threshold for percolation on a two-dimensional self-matching lattice [3]. And definitely, topological characteristics responsible for connectivity can be obtained for X-Ray computed tomography3D images, but there are certain limitations regarding resolution (≈3 µm), which can cause significant underestimation of open porosity.

- The proportion of open and closed pores based on a 3D image (micro-CT) is demonstrated in section 4.5.5, figure 4.5.41, page 81. A significant part (about half) of the porosity is attributed to closed pores. This is the result of the dominance of pores and throats, which lie below the resolution limit of micro-CT.
- Directional anisotropy of the voids has been estimated for both naturally occurred organic porosity and for the pores resulting from artificial thermal maturation. The results have been added in section 5.4.2, figure 5.4.9 (page 106) and in section 5.4.3, figure 5.4.15 (page 112). It has been observed that directional anisotropy increases with thermal maturation degree increasing due to voids formation oriented along the bedding plane in both cases.

2) *When recommending the thermal impact for particular lithotypes with particular mineral content and TOC, is it possible to estimate the effectiveness of such impact on a well scale? Is it possible to estimate how much hydrocarbons one need to burn to extract an extra ton of the "new" hydrocarbons from the rocks that look appropriate for the thermal treatment?*

The approach for estimation of the organic porosity formation effectiveness on a well and bed scales has been added in section 6.3, page 149. Besides the selection of appropriate lithotypes, it is essential to evaluate the thicknesses of each lithotype. Bazhenov Formation shales are very heterogeneous, and lithotype thickness might vary from first centimeters to several meters.

The estimation of EOR effectiveness on a well scale is one of the most crucial questions. The key processes, presented in the thesis are expected to be similar under formation conditions. However, there is one parameter, which should be considered carefully – lithostatic pressure. Lithostatic pressure might influence the void space formed during the treatment.

Regarding the question about the amount of hydrocarbons that need to be burnt to extract an extra ton of the "new" hydrocarbons from the rock that look appropriate. Kerogen is considered the main fuel for the combustion or other treatment processes in organic-rich shales. The question is broader than the thesis aims and objectives, however, this work has been done earlier in the [4]. According to the results of the mentioned work, the recovery (ratio of generated oil to kerogen, exposed to the treatment) depends on the type of high-temperature treatment: recovery for air injection is ≈24%, for hydropyrolysis ≈30%, and ≈80% for pyrolysis. In other words, we need to burn 1.3 - 4.2 m^3 of kerogen to generate 1 m^3 of oil depending on the treatment type.

Reviewer: Prof. Sergey Stanchits

1) *The thesis contains a detailed study of pore space evolution in organic matter. According to the results the precursor of organic pores is "bubble" structures. Have you analyzed the composition of the bubbles? Are they already oil? This is an important question, because this particular result contributes to the fundamental understanding of primary, very first oil generation and migration from its source - kerogen.*

The size of the "bubble" structures is in the range of 10 nm to 300 nm. An analysis of such small structures is limited by the resolution of Energy-dispersive X-ray spectroscopy in SEM (≈0.5-1 μm). These bubbles are considered as a precursor of hydrocarbons, and probably contain some oil. However, SEM showed that there is no normal oil in the bubbles on the basis of non-direct indicators. For a detailed analysis of the "bubble" structures composition, an investigation with transmission electron microscopy should be performed.

Clarification has been added to the thesis (section 5.4.4, page 116, and section 5.5, page 127-128).

2) *According to the results of the chapter devoted to the mineral matrix transformations, there are numerous alterations in mineral matrix during high-temperature treatment. Does these alterations in mineral matrix will influence mechanical properties of shales and why.*

The high-temperature treatment causes two types of alterations. The first one is chemical, which implies the decomposition of existing minerals with the formation of new crystals. The second one is physical. The thermal treatment causes the thermal expansion of minerals. There are different minerals in rock with different thermal expansion coefficients, and even crystals of one mineral types might have different expansion coefficients in different directions due to lattice anisotropy. These two types of alterations lead to the destruction of grain contacts, formation of new pores and crystals without proper cementing, and finally losing general rock integrity. All of these will result in the reduction of the ultimate strength and toughness of the rock.

3) *Are the results of PhD study applicable for other rock types (not shales), or even in other mining industries?*

The results of PhD study might be applicable in numerous high-temperature procedures associated with rock treatments. First of all, it is in-situ combustion procedures in conventional or heavy oil carbonate/clastic reservoirs, which implies similar technology in similar conditions. Other areas where results might be useful are nuclear waste storage [4], geothermal energy [5] and deep resource extraction [7], and underground coal gasification [6]. The main criterion of applicability of the results is the similarity of mineral composition.

This valuable information was added in Chapter 7 "Summary, conclusions and recommendations".

4) *Based on the results of his Ph.D. study, Tagir gave detailed recommendations that allow to select the most appropriate intervals/lithotypes for the application of technology. However, it seems to me that in the "Conclusion" section it would be good to specify – where and how can the results of his Ph.D. study be applied in Industry?*

Chapter 7 "Summary, conclusions and recommendations" has been extended by the potential application of the results in the industry (page 140-141).

Reviewer: Associate Prof. Masoud Riazi

- *"Student needs to check and correct/modify the mentioned quality of some of them (i.e., Q1)."*

Corrected. The data now is given from Scopus and SJR.

- *Some typos and errors are mentioned in the thesis file, the student is referred to the PDF file.*

Proofreading has been done. Minor typos and errors have been corrected throughout the thesis according PDF file.

- *Page 29: The name of the relevant author needs to be addressed.*

A reference to "Johnson H.R., Crawford P.M., Bunger J.W. Strategic Significance of America's Oil Shale Resource. Oil Shale Resour. Technol. Econ. 2004; II:1–33" has been added.

- *Page 33: "Decomposition of kerogen caused an internal pressure build-up enough to generate fractures in the sample" Can you add comment on additional pressure generation and break point pressure of rock?*

Kerogen density varies in the range of 1.25-1.35 g/cm3 [5, 6], whereas hydrocarbons density generally is lower and lies between 0.5 g/cm3 and 1.2 g/cm3. Considering that kerogen forms relatively enclosed layers and inclusions, and that the total mass will not change during conversion (law of mass conservation), it might be suggested that the volume of generated hydrocarbons will be higher. So, increasing of volume leads to the increasing internal pressure build-up, which results in fracture formation. However, there are no data on pressure break point value during kerogen conversion in the literature because it is challenging task to measure this pressure.

The comment has been added in the thesis text (page 18).

- *Page 35: "understanding of these alterations is essential knowledge for correct interval selection for effective high-temperature treatment implementation". Why is it essential? needs further explanation and/or example.*

A detailed explanation has been added to the text (page 20).

"Composition of shales is quite diverse and can vary significantly even within the Bazhenov Formation in term of mineral composition (carbonaceous, siliceous, and argillaceous), organic matter content (TOC content lies in wide range of 0.1-25%). EOR simulation studies do not consider mentioned diversity and different behavior of the components during the treatment, porosity and thermal conductivity are considered as constant values [75], which results in numerous biases. As well as a real application of thermal EOR in shales neglect mentioned factors [58]. However high-temperature treatment might cause different chemical and physical processes in a subsurface, which are not controlled or even understood well. These processes are related to crucial aspects of hydrocarbon production and technology application such as filtration pathways, physical (e.g. thermal conductivity) and chemical properties (gases, fluids etc.). All of these directly indicates, that understanding of these alterations is essential knowledge for accurate EOR processes simulation, effective interval selection and technology application"

- *Page 36:" There are still many open questions around the alterations in shales during heating, and a certain need for investigation exists", at this point one expects that you highlight the novelty of research.*

The novelty has been highlighted as follows.
"The thesis is intended to expand knowledge on the behavior of different shale lithotypes during high-temperature treatment on the example of Bazhenov Formation shales. Particularly, alterations of the key shale components in terms of microstructure, chemical composition, and physical properties with a focus on pore space during high-temperature treatment."

- *Page 53: "OM pores are often considered as a result of thermal maturation [92]," Is it the only likely reason for OM pores? Is there any proposed correlation between initial porosity of OM and thermal maturation or other parameters?*

Thermal maturation is considered as a major factor influences on a pore space [5–7]. The other factors are rock fabric, organic matter content, organic matter type. The influence of each factor is considered in the sections 5.1 and 6.2 in the chapter devoted to the organic matter. The influence of thermal maturation has been studied in details (sections 5.4.2 – 5.4.5). There are certain correlations proposed by different researchers [8–11], and normally this correlation suggests porosity increasing with thermal maturation level increasing, however there opposite point of views exist [12].

- *Page 53: "The occurrence of a such porosity types of in shales is still the object of debate, and there is a certain need for deeper study.", Please indicate in the text that if you will study it or future work and other researchers need to study it.*

Clarification has been added:
"Chapter 5 addresses this issue and reveals important aspects of organic porosity across natural thermal maturation gradient and its formation during artificial maturation (thermal treatment)".

- *Figure 3.3.8: Is not it due to different composition in OM? You may use higher resolution images such as those in Figure 3.3.4*

Figure 3.3.8B has been replaced by 5 times higher resolution (magnification) SEM image, which also show only single organic pores. The main reason behind single pores in OM is low level of OM maturity.

- *Page 57: Nitrogen or Helium?*

Corrected. Combustion tube was pressurized and preheated by helium.

- *Page 68: Reader expects that you add information about the mechanisms of formation of different elements.*

The processes and mechanisms behind observations in Chapter 4 are given in Chapter 6. A clarification before the results description has been added.

- *Page 83: "With the reduction of OM, calcite was partly dissolved and cavities were formed (Figure 4.5.26A)" Dissolved in what? What is the mechanism? Please add further explanation.*

Basically, it was meant dissolved by fluid (water). The processes and mechanism are discussed in Chapter 6. A clarification before the results description has been added.

- *Figure 4.5.26: It is nice and suggested that you further discuss about the dissolution and formation of nanopore.*

The processes and mechanism are discussed in Chapter 6. A clarification before the results description has been added.

- *Figure 4.5.42: What is this big black colour in the corner of some of the images? Have you performed the preparation stage? It is suggested to briefly explain the procedures of preparing Micro CT images.*

The big black colour in Figure 4.5.42 is background outside the right edge of the sample. A brief explanation of image preparing procedure is given in the method section.

- *Figure 4.5.43: Images 3 and 4 shows that a part of open pore after temperature treatment has become closed. (Bottom highlighted pores). Can you comment on the likely reason?*

It is very complicated to recognize the same pores before and after the treatment. It is suggested that initially open pores might became closed after the treatment due to formation of new minerals such as anhydrite, wollastonite, CaS and others (section 6.3 in Chapter 6).

- *Figure 4.5.44: Can you please comment on the reason of thermal conductivity increase by temperature?*

The following comment has been added in the thesis:
"Only subsample 4C (107°C) is characterized by 10% increased thermal conductivity, which might be result of lithological heterogeneity of the sample (this lithotype is represented by carbonate lenses in clay dominated mineral matrix)".

- *Page 102: Please define Tmax in the text during the thermal process.*

T_{max} g is shown in the figure Figure 4.5.46D and described at the end of the page:
"T_{max} parameter (Figure 4.5.46D) show no changes at 107°C, which mean no changes in maturity of OM. Increase of Tmax at the 400°C indicate maturation of OM accompanied with HC generation. At the 800°C OM disappears, and evaluation of T_{max} is not possible."

- *Page 104: Corg, needs to be defined as it is the first time used abbreviation in the text.*

Corg. (organic carbon content) has been defined in the text and in "List of Abbreviations".

- *Chapter 4: In general, this chapter includes valuable and practical results as high-tech equipment has been used, however, the context is rather report-like and needs adding some explanation of the mechanism and reason for the trends and changes.*

Chapter 4 and Chapter 5 present the results of the study. Chapter 6 presents the analysis, explanation, and discussion of the results.

- *Page 119: Can bacteria live/ be active at high temperature conditions?*

Actually, bacteria cannot live or be active at those conditions. Organic pores in the intercrystalline framboid space are the result of bacterial activity during sedimentation and early diagenesis. This clarification has been added in the text.

- *Page 144: Can you please explain this type of pore (i.e. shrinkage) based on your observations and results?*

The reference to the section "5.4.2.3. Organic porosity classification", which is devoted to organic porosity classification development has been added. Shrinkage organic pores represent a discontinuity with a fracture-like elongated shape, which occur within solid OM or between OM and mineral grains.

- *Page 159: Would you add the same comment (like the one for shale) on other Rock fabrics if they play role in organic pore development and preservation?*

The conclusion has been extended (now two types of rock is considered).

"Rock fabric plays a vital role in organic pore development and preservation. It is shown that those organic-rich shales, which are characterized by interlayering of mineral components and organic matter lenticulars do not tend to preserve organic porosity. Whereas shales with patchy distributed organic matter (inclusions, lenses) demonstrate good preservation of both primary and secondary porosity."

- *Page 159: Based on the nice experimental data generated: Can you provide/propose correlation between evolution of pore space with different lithotypes, mineral composition, organic matter content, and initial porosity*

Conceptual schemes are given in the section 6.3 in Figure 6.3.2, which gives is a first approximation of relationship between evolution of pore space within different lithotypes, mineral composition, organic matter content, and initial porosity. Detailed correlations should be constructed on the basis of quantitative data obtained by high resolution techniques such as BIB-SEM and FIB-SEM, which is a matter of future research. This clarification has been added in the text (page 133).

- *Page 160: "Rock thermal conductivity reduction was 70% in the lithotypes with high organic matter content", I would suggest to add the likely reason and required explanation on this sentence.*

- Reason and explanation has been added in the conclusion. Detailed explanation is given in section 4.5.6. "Thermal properties profiling"

Page 160: It is suggested that simulation of thermal EOR using the obtained results and sensitivity studies to be added in the recommendations part.

The recommendation has been added in the recommendations part.

- *Suggestion: GC (gas chromatography) analyses of the outlet of thermal chamber at different times and stages could be also valuable to further depth the conclusions.*

Thank you for the suggestion! We will continue the study and perform complex analysis of the GC analyses.

Reviewer: Dr. Mikhail Varfolomeev

- *Some minor orthographic errors presented in the text.*

Proofreading has been done. Minor typos have been corrected throughout the thesis.

- *Author showed a detailed literature review with the focus on laboratory testing of immature Bazhenov's source rock and the changes in its petrophysical properties due to thermal treatment. Less attention was paid on the analysis of papers about oxidation behavior of organic matter and combustion.*

Literature review has been expanded to analyze behavior of oil shale during combustion and oxidation processes (page 19). The following article have been reviewed and added in the references section:

1) Sun C, Ling S, Wu X, Li X, Chen J, Jiang W. Oxidation of black shale and its deterioration mechanism in the slip zone of the Xujiaping landslide in Sichuan Province, Southwestern China. Catena 2021;200. https://doi.org/10.1016/j.catena.2020.105139.
2) Kaldas K, Preegel G, Muldma K, Lopp M. Wet air oxidation of oil shales: Kerogen dissolution and dicarboxylic acid formation. ACS Omega 2020;5:22021–30. https://doi.org/10.1021/acsomega.0c01466.
3) Basu S, Verchovsky AB, Bogush A, Jones AP, Jourdan AL. Stability of Organic Carbon Components in Shale: Implications for Carbon Cycle. Front Earth Sci 2019;7. https://doi.org/10.3389/feart.2019.00297.

4) Chen W, Zhou Y, Yang L, Zhao N, Lei Y. Experimental study of low-temperature combustion characteristics of shale rocks. Combust Flame 2018;194:285–95.
5) Chen Q, Kang Y, You L, Yang P, Zhang X, Cheng Q. Change in composition and pore structure of Longmaxi black shale during oxidative dissolution. Int J Coal Geol 2017;172:95–111. https://doi.org/10.1016/j.coal.2017.01.011.
6) Chen W, Lei Y, Ma L, Yang L. Experimental Study of High Temperature Combustion for Enhanced Shale Gas Recovery. Energy and Fuels 2017;31:10003–10. https://doi.org/10.1021/acs.energyfuels.7b00762.

Reviewer: Professor Sudarshan A. (Raj) Mehta

In accordance with the comments, the following changes have been made:

- Page numbering of the technical part of the thesis (15 first pages) has been changed to Roman
- Inappropriate use of "us" has been replaced by proper grammatical forms throughout the thesis.
- Typos in the text have been corrected.

Reviewer: Professor Nikolai Pedentchouk

- *There are a number of minor grammatical issues (particularly with subject-verb agreement) that occur throughout the thesis.*

Proofreading has been done. Minor issues have been corrected throughout the thesis.

- *'More importantly though I suggest revising Chapter 7 by including more information about the significance of the main groups of results (i.e. given as 1., 2., etc.). A summary of results is given, but it is not very clear what each of those results actually imply when using thermal methods in hydrocarbon recovery. Adding a brief statement for each group of results would be very useful before the author moves onto 'Recommendations'.*

A brief statement for each group of conclusions has been added in "Chapter 7. Summary, conclusions and recommendations". The summary has been extended by the practical significance of the results.

References

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