

Thesis Changes Log

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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: Prof. Evgeny Chuvilin

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

I would like to express my deep gratitude to all the reviewers for their important and interesting comments, questions and feedback about my thesis. In the process of writing the answers to the questions, I was able to state some points more clearly, improve the quality of the work and correct some technical flaws in the text. Such work is very useful, especially in terms of interesting scientific discussions of some points and provides an incentive and motivation to continue research after defending a PhD thesis. I really hope that the dissertation committee will be satisfied with my responses to comments and improvements in the text.

In this document, I have described in detail all my answers to the questions and showed the changes in the text. For greater clarity, the structure of my answers is structured as follows. The question from the reviewer is given in *italics*. Next comes my answer in plain font. The changes that will be made in the text of the PhD thesis will be given **in purple colour**.

The answers to the reviewers are arranged in the following order: **Zhou Xuebing, Sergeev Dmitry, Yakushev Vladimir, Seo Yongwon, Stoporev Andrey, Singh Devendra Narain, Kulakov Ivan.**

Best regards,
Zhmaev Maksim

Response to Prof. Xuebing Zhou

1. In chapter 1, the distribution and occurrence of hydrate bearing permafrost are summarized in detail. I think the author tries to emphasize the importance of hydrate bearing permafrost related research. I think author can first introduce the distribution of hydrate bearing permafrost, then the potential threat of decomposition of hydrate, at last, the necessity of gas migration of study in hydrate bearing soil.

Thank you, I agree with your opinion. In this chapter, I improved Figure 4 by adding the permafrost distribution zone to the map of the distribution of gas hydrate accumulations. In general, the distribution of natural gas hydrates with an emphasis on the cryolithozone is given in Section 2.4. Examples of detected gas hydrate accumulations in different countries are given. This section also emphasizes that violation of the thermobaric conditions of hydrate-containing rocks in the cryolithozone can lead to such negative consequences as the formation of craters of gas emission and emission of natural gas into the atmosphere. In conclusion to the chapter, it is concluded that it is necessary to study gas-dynamic processes in the cryolithozone by conducting experimental modeling in the laboratory.

2. In chapter 2, the permeability measurement of sediment and relevant soil properties were introduced. I think the author tries to point out the filtration properties of cryolithozone rocks are not well understood. In this case, it is recommended to divide the reference statements by 0 °C, which can highlight the insufficient research on the permeability of hydrate permafrost.

Thanks for your comment. Section 3.2.2 describes the existing studies on the assessment of permafrost permeability. Accordingly, in the works presented in this section, the temperature of the experiments was below 0 ° C. In this section, the author tried not to focus on the work on the study of permeability in the region of positive temperatures, which are not typical for the cryolithozone. In the conclusions to the chapter, the author notes that there have been few studies on the permeability of ice and hydrate-containing sediments in conditions of negative temperatures to date, which requires additional research. The author also added a conclusion to sub-chapter 3.2.2.

The addition of the text at the end of section 3.2.2:

Thus, to date, there is a limited number of research papers devoted to the study of the permeability of ice-bearing rocks. At the same time, many works consider the water permeability of sediments at temperatures close to thawing temperatures, when in addition to ice there is a significant amount of unfrozen water in the pore space. Hydrocarbon pollutants (diesel fuel, kerosene) are also used as a fluid to solve environmental problems. There are practically no works in which gas is used to assess gas permeability. In this regard, an urgent task is to develop equipment and conduct experimental modeling of gas filtration in ice-containing rocks under thermobaric conditions characteristic of the cryolithozone.

3. In chapter 3, the basic properties of natural soil samples were tested, including composite, particle size and water saturation. The custom designed filtration unit was also described in detail. How did the author determine the porosity of the soil samples? Did you make any repeated test to each experimental run?

Thank you for this question. The porosity of the samples was determined based on formula 29, presented in the text of the dissertation. For this formula, the values of the density of solid particles and the density of the soil skeleton (dry density) were used. The density of the soil skeleton was calculated based on the mass, size

and water content of the sample. When using a core holder with comprehensive crimping, we measured the porosity of the samples before and after filtration tests. In the case of a core holder with uniaxial compression, we have the ability to control the linear dimensions of the sample in order to obtain density and porosity values at any time.

The calculation of the porosity of samples according to formula 29 is also given in the works:

Chuvilin, E.; Zhmaev, M.; Grebenkin, S. Gas permeability behavior in frozen sand controlled by formation and dissociation of pore gas hydrates. *Geosciences (Switzerland)*, 2022, 12, 9, 321.

Chuvilin, E.M.; Grebenkin, S.I.; Davletshina, D.A.; Zhmaev, M.V. Influence of hydrate formation on gas permeability variations in frozen sands. *Earth's Cryosphere*, 2020c, XXIV, 2, 34–40.

Chuvilin, E.; Grebenkin, S.; Zhmaev, M. Gas flow in frozen hydrate-bearing sediments exposed to compression and high-pressure gradients: Experimental modeling. *Cold Regions Science and Technology*, 2024, 228, 104310

4. What is the definition of equation (23), (24), (30) and (31)?

Thanks for this comment, I have made corrections and rewritten these equations in a more understandable way, adding links. I also corrected the numbering of the equations, since the number 30 was repeated twice.

The mass of water ($m_{w(h)}$, g) used to form hydrate can be determined by the following formula (Chuvilin et al., 2022):

$$m_{W(H)} = \Delta m_G * 6,47(2,5), (23)$$

where Δm_g is the difference in the mass of the gas at the beginning and end of hydrate formation or dissociation, g.

The mass of hydrate (m_h , g) can be determined by the formula (Chuvilin et al., 2022):

$$m_H = \Delta m_G * 7,64(3,5), (24)$$

The ice saturation of hydrate-saturated sample (S_i , %), i.e. the degree of filling of the pores with ice, was calculated using the formula (Chuvilin et al., 2020c, 2022):

$$S_i = \frac{(W-W_h)*\rho_d*100\%}{0,92*n}, (30).$$

If the test sample is frozen, but not yet saturated with hydrates, equation (11) is used to determine S_i .

The velocities of longitudinal (V_p , m/s) and transverse (V_s , m/s) waves were calculated in special software from EcogeosProm LLC. The calculation in this software is based on the use of the following formulas, which are used in standard documents (analogous to ASTM standards) in Russia (GOST 21153.7-75):

$$V_p = \frac{l}{t_p - t_d}, (31)$$

$$V_s = \frac{l}{t_s - t_d}, (32)$$

5. In chapter 5, the equations used for permeability test are recommended to be provided in detail. Did the author consider the viscosity change of methane in different temperature and pressure?

Thank you for this comment. The formula for determining gas permeability is taken from API RP 40. (Recommended Practices for Core Analysis. API, Washington DC, USA, 1998, 200 p) And the calculations were carried out on the basis of the pulse decay method, which is presented in the same place. The dynamic viscosity of the gas for specific conditions was also taken from the reference tables. It is worth noting that in the operating temperature range from -10 to +1°C The change in dynamic viscosity is small. Unfortunately,

at this stage I can no longer make significant changes to the text of the dissertation. The corresponding references to the works where this approach was used were given in the description to formula 34.

6. In chapter 6, how did the author get a transition of 42% of the pore ice to hydrate? How did the hydrate distribute in frozen rocks? Fig. 46 is not easy to read? The unit should be included in brackets.

Thank you for the important question on hydrate formation. The formation of methane hydrate in the studied samples began at a temperature of $-5\text{ }^{\circ}\text{C}$, when the sample was already frozen. The methane pressure during hydrate formation was in the range of 3.5 or 5 MPa (depending on the core holder used), which is higher than the equilibrium conditions of hydrate formation. So author used the excess gas method. To estimate the kinetics of pore hydrate accumulation at each time point, the parameters of hydrate content were determined using the PVT method described in Chapter 4. By reducing the pressure of methane in the sample, we calculated the amount of hydrate formed and, accordingly, the hydration coefficient or the degree of transition of pore moisture into hydrate. Since hydrate is formed from ice, its distribution corresponds to the distribution of ice. In this case, the gas hydrate occurs directly on the surface of the pore ice, which does not cause moisture migration processes and contributes to the production of hydrate-containing samples with a uniform distribution of pore hydrate. For example, according to a similar scheme, hydrate formation was carried out in the works:

Davletshina, D.; Chuvilin, E. Estimation of potential gas hydrate formation in finely dispersed soils at negative temperatures: experimental modeling. *Earth's Cryosphere*, 2020, 4, p. 23-29.

Chuvilin, E.; Grebenkin, S.; Zhmaev, M. Gas permeability of sandy sediments: Effects of phase changes in pore ice and gas hydrates. *Energy and Fuels*, 2021a, 35(9).

The author also corrected the caption to Figure 46.

When CH_4 hydrate was formed under conditions of negative temperature Celsius (-5°C) in the FS1 sample at an initial methane pressure of 5 MPa...

Figure 46. The effect of the degree of transition of pore moisture into CH_4 hydrate (K_h , u.f. – unit fraction) on the effective gas permeability and on the voidness ($100-S_{\text{tot}}$, %) of the FS1 sand sample ($P_{\text{CH}_4} \approx 5\text{ MPa}$).

7. In chapter 6, the explanation to permeability change in $\text{CH}_4\text{-CO}_2$ replacement was based on the assumption that hydrate did not migrate in pores. Did you consider the hydrate migration that block the pore throat?

In this case, the author did not consider the possibility of migration of hydrate particles in the pore space of the soil, since initially methane hydrate was formed from ice in the frozen sample, while the ice was evenly distributed over the sample. During the replacement of $\text{CH}_4\text{-CO}_2$, which was carried out at a temperature of $+1\text{ }^{\circ}\text{C}$, CO_2 hydrate was additionally formed from residual moisture in the pore space, which, according to our data, was also not redistributed. This generally led to a decrease in gas permeability. After completing the experiment, the author cut each sample in layers and determined the water content with an interval of 1 cm. Moisture redistribution was not recorded in any of the sample sections in all samples. Thus, we assume that at a positive temperature, CO_2 hydrate was also formed uniformly and there was no formation of so-called "hydrate caps" in the end parts of the samples.

8. The figures should be improved which cannot be understood at first sight.

Thank you, I took this remark into account and tried to improve the quality of the figures in the dissertation.

9. The abstract needs more data to support your major conclusions. What about the experimental method, running conditions and variation range of permeability?

Thank you for this comment. Unfortunately, according to the recommendations of dissertations at Skoltech, the abstract is limited in volume and the recommended volume should be within 400 words. Initially, I wanted to add more information to the abstract, but then I had to reduce it. At the moment, my abstract even slightly exceeds this volume.

10. In chapter 1, the goal should stress the permafrost. This may be the novelty of your thesis.

I agree with your wish. That is why considerable attention in Chapter 1 is paid to the distribution of gas and hydrate-containing deposits in the permafrost zone. This is especially true in the last section, which describes the options for the formation of gas hydrates in frozen and freezing sediments and gas dynamic processes that can lead to the formation of gas emission craters.

Response to Prof. Dmitry Sergeev

1. When formulating the conclusions, the author does not always link the obtained patterns with his own conceptual explanation of their causes. In particular, conclusion 3.1 on page 201 is of the nature of a statement without explaining the nature and causes of the observed effect. It should be explained what the found dependence is connected with.

I agree with your remark that some conclusions are sometimes presented in brief form. For conclusion 3.1, I made an additional explanation in the text.

In this case, a significant decrease in the gas permeability of the samples after injection of pure CO₂ (without nitrogen addition) was apparently due to the dominance of the processes of new formation of CO₂ hydrates, rather than the process of hydrate replacement of CH₄-CO₂.

2. Conclusion 5.4 (p. 202) should be clarified and commented on. Is the decrease in longitudinal wave velocities an unambiguous characteristic of the content of unfrozen water and evidence of changes in permeability? Is the permeability of the medium unambiguously related to the water content in the liquid phase? Probably, this is also due to the nature of the pores and deformations of the sample (Figs. 11 and 17).

Thank you for noting these dependencies. In these experiments, the determination of gas permeability and measurements of longitudinal waves began in frozen areas at a temperature of -10 °C, followed by heating to -1 °C. Under such conditions, a decrease in ice in the pore space and an increase in unfrozen water began. The graphs of the unfrozen water content for these soils are shown in Fig. 33, and the V_p changes from W_{uf} in Fig. 40. Since ice occupies a larger volume of pore space than water, the voidness of the pore space increased during its transition to unfrozen water, which affected the increase in filtration due to the expansion of filtration channels. The decrease in V_p in this situation is also associated with a decrease in the ice content, since ice has high longitudinal wave velocities. Therefore, when heating a frozen sample, we noted both an increase in gas permeability and a decrease in longitudinal waves.

Thus, the permeability of frozen samples in these experiments was directly related to the content of unfrozen water in them.

Regarding the deformations of the samples, in this case the relative linear deformations did not exceed 1%, which in the calculations practically did not affect the change in porosity (~0.01 u.f.). Significant deformations affecting the change in porosity will occur after reaching the thawing temperature, which for these samples is within (-0.2°C...-0.3°C).

“...Thus, a decrease in ice in the pore space of the samples during heating led to an increase in gas permeability due to an increase in channels through which filtration is possible since water occupies a smaller volume than ice. An increase in the content of unfrozen water at the same time led to a decrease in longitudinal waves, since the ice content in the pore space decreased.”

3. Attention is drawn to some inconvenience in the perception of figures when the illustration and the caption are broken (Figures 10, 15, 23, 44, 48, 49). Similarly, the inconvenience is linked with the tearing the header of the table and its content (Tables 5, 8, 13, 38). Parts of Figure 7 do not have the designations "a" and "b".

Thank you for pointing out these inaccuracies. For Figure 7, I added the appropriate indexes. I also tried to make sure that the figures and headings were not split from each other.

4. It is also recommended to adhere to a single style of writing formulas. Either write in words or in mathematical symbols (p. 61 and following).

Thank you for pointing out this inaccuracy. I have edited all the formulas to a single style.

Response to Prof. Vladimir Yakushev

1. *Abstract. Cryolithozone contains gas also in water-dissolved form and in adsorbed/absorbed form (coalbed methane, shale gas).*

Thank you for this comment, I completely agree. I made a clarification in the abstract:

The cryolithozone accumulates significant volumes of natural gas, both in free form and as gas hydrates. In addition, the gas in the cryolithozone can exist in dissolved form and adsorbed form if it is found in coal seams or shales.

2. *Abstract. Technogenic hydrate formation in the downhole zone can occur not only in Arctic gas fields.*

I agree with your comment. But in this case, my PhD thesis implied the Arctic region with its characteristic thermobaric conditions.

3. *Introduction. Again, other forms of existence of natural gas in permafrost are not indicated.*

I completely agree with the comment. I have added additional information to the text. I also added new literary references.

...Natural gas in permafrost can also exist in dissolved form and adsorbed form if it is found in coal seams or shales (Chuvilin et al., 2005; Yakushev, 2015).

4. *Introduction. Leak of references to publications of Dr. Gilichinsky et.al (1992-1997), where microbial gas concentration at the bottom of seasonal thawing layer (depth 0,5 -3 m) as result of seasonal freezing was studied. These depths are shallower than indicated in the thesis.*

Thanks for your comment. Regarding the depths mentioned in the introduction, there was apparently an error in the translation from Russian into English, since a more correct text would look like this: “In some cases, gas accumulations may be located at shallow depths up to the first tens of meters from the surface...” This does not contradict the depths indicated in your comment.

In this section, I initially mentioned only one publication where Dr. Gilichinsky was a co-author: Rivkina, E.M.; Kraev, G.N.; Krivushin, K.V.; Laurinavichus, K.S.; Fyodorov-Davydov, D.G.; Kholodov, A.L.; Shcherbakova, V.A.; **Gilichinsky**, D.A. Methane in permafrost of Northeastern Arctic (Published in Russian). *Earth's Cryosphere*, 2006, 10. 23–41.

I also added several other publications with his participation:

Rivkina, E.; Shcherbakova, V.; Laurinavichus, K.; Petrovskaya, L.; Krivushin, K.; Kraev, G.; Pecheritsina, S.; **Gilichinsky**, D. Biogeochemistry of methane and methanogenic archaea in permafrost. *FEMS Microbiol Ecol.*, 2007, 61, 1, 1-15. <https://doi.org/10.1111/j.1574-6941.2007.00315.x>

Rivkina, E.; **Gilichinsky**, D.A.; McKay, C.; Dallimore, S. Methane distribution in permafrost: evidence for an inter pore pressure methane hydrate. In: Paepe, R.; Melnikov, V.P.; Van Overloop, E.; Gorokhov, V.D. (eds). *Permafrost Response on Economic Development, Environmental Security and Natural Resources*. NATO Science Series, 2001, 76, 487-496. https://doi.org/10.1007/978-94-010-0684-2_33

5. Chapter 2. p.38 "Outside the GHSZ, gas hydrates cannot form, but can exist in a metastable state even at shallow depths in the form of relict hydrates..." - sentence is not completely correct. Hydrates can form in permafrost zone outside current GHSZ in places, where local GHSZ can appear for a short period due to geodynamic processes like talik zone freezing.

I agree with your comment. I have made some additions to the text:

However, in some cases, small local stability zones of gas hydrates may occur in the cryolithozone due to the influence of geodynamic processes. For example, this is possible when a gas-saturated talik freezes, which eventually leads to cryogenic gas concentration and the formation of gas hydrates, which is described in section 2.4 (Yakushev, Istomin, 1992; Yakushev, 2009; Chuvilin, Davletshina, 2018).

6. Experimental chapters. How effective PEEK polymer material prevents gas slippage along sample/holder wall contact when filtration experiments?

The core holder of the filtration unit with a central part made of PEEK material has proven itself well enough during filtration tests. The most important feature of this core holder is the presence of a compression (uniaxial compression) system. In such installations, the tightness of the sample is achieved due to the lateral expansion of the sample under the action of axial load, as well as due to the freezing of the sample with the walls of the core holder, which prevents gas slippage.

For comparison, we performed gas purging of a frozen impermeable loam sample in an all-metal pressure chamber without the possibility of crimping under heating conditions. After removing the sample from the pressure chamber, furrows were found on the sample along the walls, which indicated passage between the wall of the pressure chamber and the sample. When using a core holder with uniaxial crimping, no such problems were observed. The studies carried out with the help of this core holder have already been published in articles:

Chuvilin, E.; Grebenkin, S.; Zhmaev, M. Gas flow in frozen hydrate-bearing sediments exposed to compression and high-pressure gradients: Experimental modeling. Cold Regions Science and Technology, 2024, 228, 104310, <https://doi.org/10.1016/j.coldregions.2024.104310>

Chuvilin, E.; Grebenkin, S.; Zhmaev, M. Experimental modeling of gas filtration in frozen and hydrate-containing rocks under uniaxial compression conditions. (Published in Russian) Earth's Cryosphere, 2024, 28, 6, 31-44.

7. Table 12 - incomplete mineral composition for Sand 1 and Sand 2. No stratigraphic index for Polymineral loam.

Thank you for these comments. Regarding sand 1, according to the latest data, the quartz content in it is more than 98%. I took the value of 90% from my earlier work, which was within the framework of a master's degree: Chuvilin, E.M.; Grebenkin, S.I.; Zhmaev, M.V. Impact of hydrate and ice formation on gas permeability of sandy soils (Published in Russian). Vesti Gazovoy Nauki scientific-technical collection, 2018, 3(35), 264-273.

I indicated the mineral composition of sand 2 incorrectly, confusing it with other sand. I have made corrections to table 12 in the text. I also added a stratigraphic index for the polymineral loam:

Table 12...

Sand 1	mJ ₃	Lyubertsy	> 98	quartz
Sand 2	mQ ₃	South Tambej gas field (Yamal peninsula)	93.7	quartz
			5.1	albite
			1.2	orthoclase

Polymineral loam	m P ₁₋₂
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This loam is confined to Paleogene deposits of marine genesis (m P₁₋₂) (Bogoyavlensky et al., 2021a).

8. *No information about sands washing and dewatering before experiments. No data about residual pore water salinity in natural samples. No data about pore water freezing/thawing temperature in prepared samples.*

Thank you for this clarification. Regarding the preparation of soil samples, sand washing was not carried out, since it had a low salinity. I added the salinity values for the soils used to Table 13.

The data on the thawing temperature were presented in the corresponding sections of Chapter 5. For example, in section 5.2 under Table 24: “For a sample of natural loam, the thawing temperature was (T_{th}) -0.1 °C, and for a model sand-clay mixture T_{th} = -0.2 °C.” For a mixture of sand and kaolinite, information on the thawing temperature has been added in section 5.1: “At the same time, the thawing temperature of the sand-clay mixture with kaolinite was -0.1 °C, which is higher than the temperatures at which the gas penetrates through the frozen samples.”

9. *Figure 24. Such experiments need to be repeated few times to receive statistics about temperature of filtration start.*

I agree with your comment. These experiments turned out to be quite laborious and time-consuming, but they provide a good foundation for further research. In the future, these works will be continued and expanded within the framework of RSF projects.

10. *No information about pressure gradient values along samples in the section "5.1 Effect of the gas pressure gradient on gas filtration in ice-bearing frozen sediments"*

Thanks for this clarification. Although in section 4.3.1 of the methodological chapter I mentioned that the crimp pressure in these experiments exceeded the gas pressure by 1 MPa, in order to prevent gas leakage from the rubber cuff into the hydraulic system, I supplemented the description in section 5.1. At the same time, the gas pressure on the initially impermeable frozen samples at the inlet was 1, 2 and 4 MPa.

At the same time, the crimp pressure around the frozen samples was set in such a way as to exceed the gas pressure by 1 MPa. This was done to prevent gas leaks into the hydraulic system from the rubber cuff.

11. Figure 33. How these results were obtained? No explanations in text.

Thank you for this important clarification. The amount of unfrozen water for the soils used was obtained by the author of the water-potentiometric method using the WP4-C device. I have made the appropriate additions to the text.

To analyze the phase composition of moisture in frozen soils, the activity of pore moisture was measured using the Decagon WP-4 device and the dependence of the unfrozen water content on temperature was constructed (Figure 33) using the potentiometric method (Chuvilin et al., 2020c).

12. In Chapter 6, where experimental assessment of the gas permeability of sediments under conditions of formation and decomposition of pore hydrate and ice, no data about hydrate textures formation during gas hydrate formation in sandy samples. Although author mentioned about hydrate textures formation when hydrate formation in sandy sediments (p.70) it is not clear: was hydrate textures formation took place in the experiments on permeability measurement or not. And, if yes, how it reflects in gas permeability of sample.

Thanks for your comment about hydrated textures. In the experiments given in Chapter 6, hydrate formation began in frozen sandy samples at a negative Celsius temperature at pressures of the hydrate-forming gas above equilibrium values. With this scheme, the hydrate was formed from already formed ice. All sand samples had a massive cryotexture, respectively, after hydrate formation, the samples had a massive cryohydrate texture when the hydrate was evenly distributed throughout the sample.

13. In section 6.3 where CH₄ / CO₂ replacement process is studied, there is no data about CO₂ dissolution in pore water during experiments, especially when temperature conditions are close to 0⁰C.

Thanks for your comment. I corrected this inaccuracy by adding information in methodological chapter 4 about taking into account the solubility of CO₂ during calculations. To account for solubility, V.A. Istomin's calculations were used, carried out according to the Krichevsky-Kazarnovsky formula (Istomin, 1999; Istomin, et al., 2018).

A similar method was taken into account, for example, in the work: Chuvilin, E.M.; Guryeva, O.M. Experimental investigation of CO₂ gas hydrate formation in porous media of frozen and freezing sediments (Published in Russian). Earth's Cryosphere, 2009, 13, 3, 70-79.

For experiments involving CO₂, its solubility in water was also taken into account (Chuvilin Guryeva, 2009). The values of the solubility of CO₂ were obtained based on calculations by V.A. Istomin using the Krichevsky-Kazarnovsky equation (Istomin, 1999, Istomin et al., 2018).

Response to Prof. Yongwon Seo

1. In Chapter 4, the candidate should specify the rationale for using a CO₂ (55%) + N₂ (45%) gas mixture to simulate flue gas. Typically, the CO₂ concentration in flue gas ranges from 10 to 20 %.

Thanks for your comment. I completely agree with your statement that in most cases the concentration of CO₂ in flue gases reaches 20%. In our case, we used a gas mixture of CO₂ (55%)+ N₂ (45%), since it allowed us to work with a gas pressure of 4 MPA for the stable existence of CO₂ hydrates at +1 ° C. In addition, this is more satisfactory for the conditions of the cryolithozone of the north of Western Siberia. A decrease in CO₂ concentration and an increase in N₂ leads to an increase in gas pressure, which is supplied to the core holder in order for CO₂ hydrate to exist. We tried to work with a 30/70% CO₂/N₂ mixture at a pressure of about 7 MPa and we noticed deformation of the rubber cuff and gas leakage into the hydraulic system, which led to the experiment stopping. Therefore, we settled on a mixture of CO₂ (55%) + N₂ (45%) in order to minimize technical problems and work at a lower gas pressure.

I have made additions to chapter 4:

In these experiments, a flue gas mixture consisting of 55%CO₂ and 45%N₂ was selected because it allowed working with a gas pressure of 4 MPa for the stable existence of CO₂ hydrates at +1 ° C. A decrease in the concentration of CO₂ and an increase in N₂ in the flue mixture leads to an increase in gas pressure, which is supplied to the core holder in order for CO₂ hydrate to exist. At the same time, the risk of gas leaks from under the rubber cuff into the hydraulic system increases, which leads to the shutdown of the experiment and long-term cleaning of the equipment. In this regard, mixtures with a high nitrogen content requiring high gas pressures were not used in these experiments.

2. P123, in eq (21), how did the candidate determine “compressibility factor” Z? Was it calculated using equation of states or obtained from data tables?

Thank you for this important question. The values of the compressibility coefficient were taken from reference tables, for example, presented in API RP 40. Recommended Practices for Core Analysis. API, Washington DC, USA, 1998, 200 p.

3. P124, the candidate used a density of 0.794 g/cm³ for CH₄ hydrate and 0.788 g/cm³ for CO₂ hydrate. However, these values are significantly lower than those reported in the literature. While density values can vary slightly depending on temperature, pressure, and the degree of cage occupancy, the typical density of CH₄ hydrate is 0.91 g/cm³, and that of CO₂ hydrate is 1.11 g/cm³.

You are completely right about the density of methane and the density of CO₂. In this case, equation 27 for hydrates considers ρ_h - crystallographic density of an empty square lattice (without gas molecules by analogy with the pure ice structure), which will be lower than just the hydrate density. Such values, for example, were used by our scientific group in the works:

Chuvilin, E.M., Bukhanov, B.A., 2017. Effect of hydrate accumulation conditions on thermal conductivity of gas-saturated soils. Energy and Fuels 31 (5), 5246–5254. <https://pubs.acs.org/doi/10.1021/acs.energyfuels.6b02726>

Chuvilin, E.; Grebenkin, S.; Zhmaev, M. Gas permeability of sandy sediments: Effects of phase changes in pore ice and gas hydrates. Energy and Fuels, 2021a, 35(9). <https://doi.org/10.1021/acs.energyfuels.1c00366>

I have made a correction to the description of equation 27:

ρ_h - density of the empty framework of the hydrate crystal lattice (without gas molecules by analogy with the pure ice structure) (g/cm³). In calculations, the ρ_h of methane was assumed to be 0.794 g/cm³, and the ρ_h of carbon dioxide hydrate was 0.788 g/cm³ (Chuvilin, Bukhanov, 2017).

4. In Chapter 6, for CH₄-CO₂ replacement, given that the initial saturation of the hydrate sample is relatively low, the impact of additional CO₂ hydrate formation from residual water appears to outweigh the effect of actual guest replacement on gas permeability. If feasible, it would be beneficial to evaluate these two factors (additional CO₂ hydrate formation and actual guest replacement) separately by comparing and analyzing hydrate saturation (S_h) values before and after CO₂ injection.

Thanks for your comment. In this case, in experiments with injection of pure CO₂, it seems that the process of formation of CO₂ from residual pore moisture plays a more significant role than the replacement process, which is noted in the decrease in gas permeability of samples during the experiment. The graph for S_h will be similar to the graph K_h shown in Fig. 56 from which it can be concluded that the cumulative degree of filling of pores with methane hydrate and CO₂ hydrate after the start of replacement will increase, which will lead to blocking of filtration channels and a decrease in gas permeability. However, a detailed study of the replacement process is planned to be carried out as part of further research and new filtration experiments, which will be a continuation of this research work.

Response to Prof. Andrey Stoporev

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.

Thank you for this detailed comment. I totally agree with that. Unfortunately, the abstract, according to the requirements, should have a limit of 400 words, and at the moment it already has more than 400 words, but I tried to supplement it a little:

During such emissions, a significant amount of greenhouse gases can enter the atmosphere, in addition, the formation of gas emission craters in areas with developed infrastructure of the fuel and energy complex can lead to serious catastrophic consequences.

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.

Thank you for this clarification. I have added some additional paragraphs to the text of the dissertation in chapters 5 and 6.

To chapter 5: In this chapter, based on experimental modeling, an assessment of critical temperatures and gas pressures is carried out at which gas can break through the thickness of frozen rocks with the formation of gas emission craters when thermobaric environmental conditions change caused by various factors. The role of changes in the phase composition of pore moisture and structural deformations on changes in the filtration characteristics of the studied soil samples was also studied. The results of these studies can be applied in the development of recommendations for predicting geocryological hazards associated with the occurrence of gas emission craters in Arctic areas with a developed infrastructure of the fuel and energy complex.

To chapter 6: In this chapter, based on experimental modeling, the effect of injection of inhibitor gas at a temperature of -5°C on the change in gas permeability of a hydrate-saturated sample is shown. Changes in gas permeability and the possibility of extracting methane from hydrate-containing samples during the hydrate replacement of $\text{CH}_4\text{-CO}_2$ during injection of gaseous CO_2 or flue mixture (55% CO_2 and 45% N_2) into hydrate-saturated samples were also evaluated. Thus, the potential of these experiments can be used in the development of technologies for extracting natural gas from hydrate-containing rocks in the Arctic. Studies on the assessment of permeability and relative linear deformations of frozen hydrate-containing rocks at various axial pressures are of more fundamental importance, allowing us to simulate the conditions of hydrate-containing deposits in conditions of stable existence of the ice component at various depths.

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.

In general, I agree with your comment, but I would like to note that geologists, and in particular geocryologists, use the term negative temperature widely in scientific and educational literature, in particular in the articles mentioned in the dissertation (Chuvilin et al., 2021, 2022, 2024 and etc). I agree that when writing, you should specify the temperature scale (in my case, the temperature is negative Celsius). Also, in many cases, I additionally indicated the temperature values directly in parentheses so that it would be clear what values we are talking about.

In the text of the dissertation, I tried to make clarifications so that only "negative temperature" would not be written without an appropriate explanation.

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?

Thank you for these important questions. The model samples, in general, in terms of dispersion, porosity and the degree of pore filling with ice and hydrates, are close to real cores, since not only sands, but also sandy loams and loams are suitable for potential gas collectors and gas hydrates. The basis of the model samples was quartz sand, to which clay particles were added to match sandy loams or loams. However, in addition to the model ones, sand (also quartz and similar in granulometric composition to the model one) and loam selected from gas-producing horizons were also used. The axial load in filtration experiments was used to simulate pressure at various depths at which hydrate-containing rocks may be located. Accordingly, if we compare the permeability of samples without axial load (near-surface conditions) and with axial load (deep conditions), then the permeability of samples may differ.

These experiments are largely methodical, so it is difficult to scale these results at this stage. It is necessary to carry out work on a large number of natural samples of various compositions (preferably cores of undisturbed composition) in order to accumulate data and then interpret production tests.

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?

Thank you for this question. The soil samples were prepared in such a way that the moisture distribution in them was uniform and in the frozen state they had a massive cryogenic texture. I was based on the methodological developments that were carried out in our laboratory to obtain samples with an equilibrium distribution of ice and gas hydrate along the length of the sample (Chuvilin et al., 2019, 2022). This is achieved by preparing a ground suspension with a given amount of water (or ice chips) and thoroughly mixing it and holding it, and layer-by-layer sealing in the core holder, as described in chapter 4 of the dissertation. Even while doing the master's work, the author also conducted methodological studies on the preparation of samples and their cutting in a frozen state to analyze moisture distribution. These studies also showed high uniformity of the samples, differences in humidity when cutting the sample by 1 cm differ from each other by no more than 0.1% before filtration tests.

Chuvilin, E.M.; Davletshina, D.A.; Lupachik, M.V. Hydrate Formation in Frozen and Thawing Methane-Saturated Sediments. *Earth's Cryosphere* 2019, 23, 44–52.

Chuvilin, E., Ekimova, V., Davletshina, D., Krivokhat, E., Shilenkov, V., and Bukhanov, B. Pressure influence on salt migration in frozen hydrate-saturated sediments: Experimental modeling. *Energy and Fuels* (2022).

After filtration tests, each sample was cut into 1 cm at a temperature of -5 °C and there was no significant redistribution of humidity. Moisture loss was not observed in the samples, since gas purges were carried out at low pressures (no more than 1 bar). In some samples, in which the determination of gas permeability was completed at a temperature of +1 °C, only an increase in humidity in the final part of the sample by 3% was noted.

Thus, we assume that when determining permeability, moisture does not escape in our ice and hydrate-containing samples. Gas permeability at each stage was determined at least 3 times, while values were taken that did not differ from each other by 10%.

Regarding microtomography, the author agrees with the reviewer, however, this is planned to be implemented as part of further research that will be conducted on the basis of this dissertation and the refinement of a cell with a cryostat that can be installed in a tomograph, since we do not have the opportunity to combine a filtration unit and a tomograph in one room.

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?

In this case, the achieved constant value of gas permeability corresponds to a sample without hydrate, since after the dissociation stage in experiments, the samples are usually heated to +5 °C at atmospheric pressure and using a pressure sensor, the change in gas pressure in the system is recorded. Accordingly, in section 6.1, for the TS2 sample after such heating, an increase in CH₄ pressure was noted, indicating the presence of residual hydrate, and in the FS1 sample the pressure did not change, which indicates that the entire hydrate decomposed at the dissociation stage at -5 °C after injection of N₂.

7. All figure captions must indicate the conditions under which tests were conducted, if applicable.

Thanks for the comment, I have corrected the captions to the figures where possible.

8. In Fig. 17, you seem to confuse the gas-water interface with hydrate-water saturated with gas.

Thanks for the comment. This figure was taken from the corresponding article, which is referenced in the caption and these borders are marked there (Yang, 2015). The authors of the article rather wanted to emphasize the initial water-gas boundary, and subsequently the formation of hydrate limited the contact between water and gas, preventing further formation of hydrates. Perhaps the authors of the article should have made the arrows or the caption to them a little more precise.

Yang, L.; Zhao, J.; Liu, W.; Li, Y.; Yang, M.; Song, Y. Microstructure Observations of Natural Gas Hydrate Occurrence in Porous Media Using Microfocus X-ray Computed Tomography. *Energy Fuels* 2015, 29, 8, 4835–4841. <https://doi.org/10.1021/acs.energyfuels.5b00881>.

9. Figure 21 includes an unnamed blue line. It seems to be the water-ice equilibrium vs. pressure. Please correct.

Thank you, I have corrected this Figure.

10. In the experimental part, it is necessary to justify the choice of different pressures (3 and 4 MPa) for a substitute gas (CO₂ or its mixture with nitrogen).

Thanks for the comment, I added a clarification to the text in section 6.3:

The choice of a pressure of 3 MPa for CO₂ injection and 4 MPa for the flue mixture at +1 °C was due to the fact that such thermobaric conditions correspond to stable hydrate conditions for the gas mixtures used. Therefore, pressures were taken that would be above equilibrium conditions by about 1.5 MPa. Also, taking into account the technical capabilities of the equipment, based on previously conducted experiments with CO₂, these pressures allow you to work without gas leaks from under the rubber cuff into the hydraulic system with oil. In case of such leaks, it is necessary to prematurely stop the experiment and clean the equipment.

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.

I completely agree with your comment.

12. 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.

Thanks for that comment. As far as I understand, the following sentence in the text is meant: «When the thermobaric conditions of gas-saturated, ice- and hydrate-bearing rock state change, whether due to anthropogenic influence or natural geodynamic processes, gas accumulations with elevated pressure may form» in Chapter 2. This implies not only hydrate-containing, but also gas-containing rocks that can occur in the Arctic as a whole. If we consider hydrate-containing deposits, for example, a change in temperature towards its increase will cause dissociation of pore hydrates, as a result, significant volumes of gas can be released and concentrated under a layer of ice-containing rocks. As the gas pressure increases, for example to 2 MPa, such a gas pressure can break through the overlying frozen rocks and lead to the formation of a gas emission crater and emission of natural gas into the atmosphere.

Another option for the formation of deposits with increased gas pressure gradients in the cryolithozone is possible when the talik freezes. Such a case is described in Chapter 2 and demonstrated in Fig. 10. In this case, when the talik freezes, cryogenic compression of the gas and its concentration in the upper part of the section will begin. When significant gas pressures occur, the processes of visco-plastic deformation of the overlying rocks will begin, followed by their breakthrough and removal of gas-water and ice-ground mass to the surface with the formation of a gas emission crater. If the roof has significant power and strength, then when the pressure corresponding to the equilibrium conditions of hydrate formation is reached, local layers of gas hydrates will form, as shown in Fig. 9.

13. 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 replacement 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 are 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? Under equilibrium conditions or in HSZ?

Thank you for this comment.

When nitrogen is introduced, it competes with methane for inclusion in the hydrate structure:

Destabilization Effect: Nitrogen molecules, being smaller and having different interaction properties compared to methane, do not stabilize the hydrate lattice as effectively. As a result, the hydrate structure becomes thermodynamically less stable.

Driving Force for Methane Release: The presence of nitrogen shifts the equilibrium conditions, encouraging the release of methane from the hydrate to restore equilibrium.

Using the FS1 sample as an example, we did not achieve complete hydrate conservation, just as the gas permeability did not change as in the TS1 sample during conservation. When the dynamics of gas permeability began to decrease, we pumped nitrogen, so we did not wait until all the hydrate was self-conserved. And it was noted that after nitrogen injection, the dynamics of increased permeability increased.

Regarding the temperature of the sample. Indeed, the temperature sensor is mounted on the end part and is adjacent to the sample. When the cooled gas is supplied to the sample, no temperature changes are recorded using this sensor. Also, to check the temperature in the middle of the sample, the author tried to put a temperature sensor in the middle of the core holder, replacing the G3 pore pressure sensor with it. After the cooled gas was supplied, no temperature change was recorded in the middle of the sample either.

The experiments in section 6.1 on dissociation with subsequent injection of N₂ were carried out at a temperature of -5 °C, which corresponds to the stability of the ice component in the pore space. The sample stood at this temperature for more than 12 hours, so the temperature of the core holder and the sample was the same. Nitrogen was supplied to the sample pre-cooled, which is also indicated in the text of the dissertation. Thus, in this experiment, conditions are not created when the temperature will be slightly below 0 °C, and the ice can melt, i.e. we assume a uniform temperature distribution according to the sample.

In the CH₄-CO₂ hydrate replacement experiments in Section 6.3, the replacement was performed at a positive temperature of +1 °C, which corresponds to the absence of ice. In these experiments, we are not talking about self-preservation of hydrates, but on the contrary, we note the formation of CO₂ hydrates from residual water.

In the case of new studies at temperatures around 0 °C (for example, -0.5 °C), and the supply of warm (without pre-cooling) gas, it will be necessary to assess the temperature distribution of the sample, which is correctly noted by the reviewer.

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.

Thanks for this comment, but I can't completely agree with the reviewer.

In this paper, structural transformations were noted by determining the relative linear deformations of samples at various stages of experiments. Therefore, this item is new. In particular, in Chapter 6, data were obtained for the first time on changes in the gas permeability of hydrate-containing rocks at various axial pressures, as well as linear deformations of these samples were noted and the growth of deformations was compared with changes in permeability during the experiment. For frozen rocks, in Chapter 5, the visualization of the internal structure of the samples was carried out before and after filtration tests by conducting studies on an X-ray tomograph. The images obtained by tomography show the changes occurring with the ice sheets before and after the experiment.

These studies were largely methodical and were limited due to the employment of the tomograph by other scientific groups. In addition, the scanning of samples could only be carried out on a core holder with uniaxial compression, the body of which was made of polymer material. In the future, the author expects to study the

internal structure of ice and hydrate-containing samples on a more frequent basis, if there is access to appropriate equipment.

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?

Thanks for your comment. In the experiments given in Chapter 6, hydrate formation began in frozen sandy samples at a negative Celsius temperature at pressures of the hydrate-forming gas above equilibrium values. With this scheme, the hydrate was formed from already formed ice. There was a massive cryotexture in all the sandy samples, when the ice was evenly distributed throughout the sample. Accordingly, after hydrate formation at a temperature of -5 °C samples had a massive cryohydrate texture when the hydrate was distributed evenly throughout the sample. In this way, samples were prepared in all articles presented in the dissertation where the author participates (Chuvilin et al., 2020, 2021, 2022, 2024 and etc). This cryohydrate texture was observed by the author many times during the cutting of demonstration samples during practical classes with students at Moscow State University and Skoltech.

The formation of hydrates at the entry/exit sites or the so-called hydrate caps is usually possible with hydrate formation at a low positive temperature in poorly permeable rocks, therefore we did not work in such a thermobaric regime and with initially low-permeable deposits.

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?

Thank you for this comment. In conclusion, I tried to reflect the practical significance of this study in the 3rd paragraph, which emphasizes the importance of determining the critical temperatures and pressures at which gas breaks out of frozen strata to develop recommendations for the prevention of geocryological hazards. The results of filtration experiments with hydrate-containing rocks can be useful in choosing a method for extracting gas from gas hydrate deposits.

I also made additions to the conclusion (Chapter 7):

For example, based on the conducted research, one of such promising and environmentally friendly methods of extracting natural gas may be the replacement of methane hydrate for CO₂ hydrate when injecting gaseous CO₂ or flue mixtures (CO₂+N₂) into hydrate-containing deposits. However, a significant number of filtration tests are required in order to make the right selection of conditions to ensure the permeability of sediments so that the formation of CO₂ does not dominate the extraction of CH₄.

In the future, on the basis of this methodological work, the author plans to continue research on the permeability of ice and hydrate-bearing rocks under various thermobaric conditions.

It is planned to conduct a large number of filtration tests in order to obtain more detailed statistics on critical temperatures and pressures at which gas breaks through ice-containing deposits. Also, as soon as available, it is planned to use cores directly from Arctic regions from gas-bearing horizons with natural humidity and undisturbed composition.

Due to the appearance of a new core holder with a durable polymer body, which allows operation at higher pressures, it is planned to expand the number of works aimed at studying the hydrate replacement of CH₄-CO₂ in soil samples using flue mixtures with different ratios of CO₂ and N₂. This will help in assessing more effective substitution conditions at high temperatures, the permeability of which will not lead to a significant decrease in hydrate-containing deposits.

For a more detailed characterization of the internal structure of the samples, the distribution of ice and hydrate water in them and structural transformations, assessment of the content of unfrozen water and the effect of salinity, it is planned to use such methods as NMR and X-ray computed tomography. Thus, this creates a serious reason for additional research and participation in competitions for projects and grants with this topic.

Response to Prof. Devendra Narain Singh

1. Chapter 1. In statement of the problem, the term *Permafrost rocks* is used to explain the relevance of the present study to the real-life conditions. However, *unconsolidated sediments from Yamal Peninsula and artificial sand-clay mixtures* have been employed as the host porous media. In this context, it becomes mandatory to justify the reasons that why these materials are equivalent to the rocks.

Thanks for that comment. Yes, fine-grained sand and polymineral loam from the Yamal Peninsula are used in my work. Potential reservoirs for gas hydrates in Arctic conditions may be sandy deposits. These can be dispersed deposits – sands, sandy loams, as well as loams. There may also be cemented sandstones. In my work, only dispersed deposits are considered. Due to the limited number of natural cores of dispersed rocks on which research can be carried out, model samples were prepared. In these samples, fine-grained sand, close in dispersion to natural sand, was used as a basis, and clay particles were added in various proportions to obtain sandy loams and loams, which are widespread among dispersed deposits characteristic of the Arctic. With the help of the core holder of the filtration plant, we can set the all-round or axial pressure on our initially unconsolidated rocks, thus we achieve their consolidation, which is possible at various depths and with the help of the climatic installation we set the required temperature (positive or negative Celsius), modeling natural conditions.

2. Chapter 2. Will it be OK to modify the title of the chapter as, *Formation and Existence of Gas Hydrates in Permafrost Regions (and not the marine conditions)*.

Thanks for the comment. Yes, I changed the title of the chapter in this way.

3. It is mentioned that “*n is the number of water molecules*”, is this the hydration number?

Yes, it is a hydration number. I made a correction

4. Lines 4-6 in the first paragraph of Subsection 2.1 should be substantiated with the relevant literature.

I added the relevant literature after the sentence, although the same references are given at the end of the paragraph:

by the formula $M \cdot nH_2O$, where M is the hydrate-forming gas molecule, and n is the number of water molecules (hydration number) (Yakushev, 2008; Sloan, Koh, 2008, Wang et al., 2020).

5. Page no 29, the statement “*Due to hydrogen bonds ... attraction of van der Waals forces*”, is not clear. Hence rewrite and cite proper references.

Thanks for the comment, maybe I didn't write this sentence very clearly in English, I rewrote it in a different way:

The cage lattice of gas hydrates is formed by water molecules (host molecules) due to hydrogen bonding. Inside this lattice there are cavities that are occupied by guest gas molecules. Gas molecules are bound to host molecules by van der Waals forces (Sloan, Koh, 2008; Carrol, 2020; Wang et al., 2020).

6. With reference to Figure 3, huge variations are observed in the Pressure (P) and Temperature (T) conditions favourable for the formation of hydrates with different gases. However, the explanation in this context is missing and should be included.

Thanks for the comment, I added the information after Figure 3:

Different gases form gas hydrates at different pressures and temperatures due to their physical and chemical properties, as well as interactions between gas molecules and the hydrate framework. The main factors determining such differences are: the size of the gas molecule, the polarity of the gas molecule, the solubility of the gas in water, thermodynamic stability, and the type of hydrate structure (Istomin, Yakushev, 1992; Makogon, 1997; Sloan, Koh, 2008).

7. *“With a decrease in temperature, thermal conductivity of hydrates will decrease” (Refer Page No: 32). Explain this phenomenon.*

In this sentence, I made a mistake, because I originally meant hydrate-containing deposits (i.e., not only hydrates, but ice and unfrozen water in the pores) under freezing conditions, when as unfrozen water passes into ice and then into hydrate, thermal conductivity decreases. I wrote about the thermal conductivity of hydrate-containing deposits further after Table 1 and provided links to relevant works (Chuvilin, Bukhanov, 2014, 2017). I deleted this sentence in the text of the dissertation.

8. *Replace the word weaker with minor on Page No: 33.*

Thank you, I replaced this word in the text.

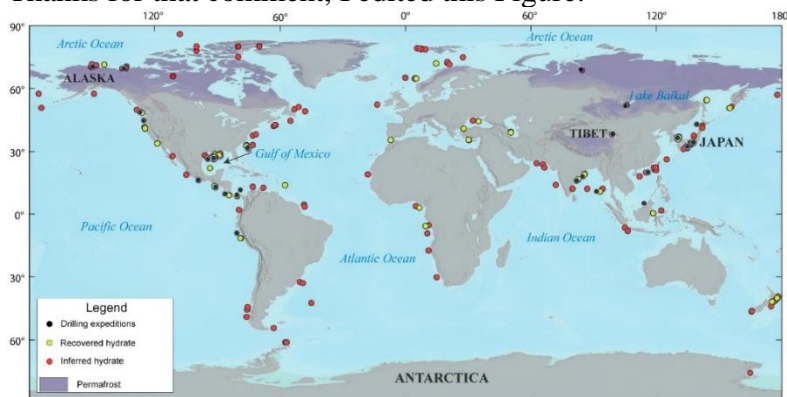
9. *Explain the relevance of comparing the properties (refer Table 1) of hydrates and ice to the present study by including a separate paragraph. How these properties would be relevant to the present study?*

I have added an additional paragraph to the text with an explanation:

Comparing the properties of hydrates and ice is important for research related to the study of hydrate-containing sediments that may be located in the cryolithozone. Both of these compounds have a similar aqueous crystalline matrix, but differ in their chemical composition, physical, mechanical, and thermophysical properties. When conducting comprehensive studies, which will include not only the determination of permeability, but also, for example, the determination of the velocities of longitudinal and transverse waves, thermal conductivity, knowledge of such characteristics will make it more likely to distinguish hydrate-containing deposits from deposits without hydrate.

10. *Figure 4 presents distribution of gas hydrates in both marine conditions and permafrost regions. However, it is better to modify the figure by highlighting the permafrost regions as the present study is relevant to the hydrates in the presence of ice.*

Thanks for that comment, I edited this Figure:



11. Provide a detailed explanation to elaborate the difference between Figures 8a & 8b and Figures 9a, 9b and 9c.

Thanks for your comment. The main difference is in the scale of what is happening. Figure 8 shows the long-term epigenetic freezing of the rock formation. There may be gas-saturated deposits in this formation, which will be limited by poorly permeable rocks-fluid barriers. As a result of such freezing, gas-saturated deposits become hydrate-containing when appropriate temperatures and pressures are reached.

In the case of Figure 9, the freezing of the talik is shown there. Such a situation is possible in near—surface conditions, and is more limited in scale than for Figure 8. Talik is a section of non-freezing rock among permafrost. Thus, when such a limited area is frozen, surrounded on all sides by frozen rocks, cryogenic compression and concentration of gas is possible, if it is there in sufficient quantities. When the equilibrium conditions of hydrate formation are reached, small layers of gas hydrates will form.

The addition in the text:

Thus, such local layers of gas hydrates can be located in near-surface conditions significantly higher than the depths of 200 m described in Figure 8 (Yakushev, Istomin, 1992; Istomin et al., 2020).

12. Figure 10 and its explanation is not clear and hence do the needful.

I have made changes to the text, expanding the description of Figure 10:

Similar taliks can form under lakes in the Arctic (Fig. 10 (I)). The gas in these taliks will be of biogenic origin and, in the case of inflow from deeper horizons, may be thermogenic. After the lake dries up, the freezing of this talik may begin, while after the freezing of its roof it will become closed (Fig. 10 (II)). The freezing of the talik will continue from above and from the sides (Fig. 10 (III)) and in such systems, cryogenic squeezing of gas into the upper part of the talik is possible, and as it freezes, the gas pressure will increase, which will lead to the formation of a positive relief form - a pingo-like structure (Fig. 10 (IV)). The gas pressure can reach a certain critical value, at which the processes of viscous-plastic deformation of the overlying rocks will begin, followed by their breakthrough and the removal of gas-water and ice-soil mass to the surface with the formation of a gas emission crater at the site of a previously formed pingo (Fig. 10 (V-VII)). And then this crater will fill with water, forming a lake (Fig. 10 (VIII)) (Chuvilin et al., 2020a,b).

13. Chapter 3. Much of the information related to the basics of gas hydrates and the methods to measure the porosity & permeability of the rocks is available in the standard textbooks. Hence, it is suggested to merge Chapters 2 and 3 (to develop a single chapter on literature review) by highlighting the gas hydrate distribution in permafrost regions/frozen areas and permeability measurements performed in case of the hydrate bearing sediments in the presence of ice, which should be the basis for the development of the experimental methodology presented in the upcoming chapters.

Thank you for such a detailed comment. Despite the fact that I cannot make significant changes to the text of the PhD thesis and combine chapters by changing the structure of the work, I will try to explain the logic of this breakdown. Chapters 2 and 3, despite being a literary review, were divided in meaning. Chapter 2 provides general information about gas hydrates, comparing the properties of hydrates and ice, and the distribution of hydrates in the world with an emphasis on the cryolithozone and gas dynamic processes in Section 2.4.

Chapter 3 provides a direct overview of the methods used to study filtration-capacitive hydrate and ice-containing rocks and provides relevant experimental work that exists at the moment. The main focus of this work, as noted in the goals and objectives of the dissertation, is related to the experimental modeling of gas filtration in ice and hydrate-containing rocks at subzero temperatures. Chapter 3 highlights the insufficiency of existing works that consider the permeability of hydrate-containing sediments at subzero temperatures,

when an ice component can stably exist in the pore space of rocks. That is why Chapter 3 is larger and more meaningful than Chapter 2.

14. As the ice and hydrate bearing sediments are highly impermeable as compared to their host sediments and/or rocks, and the permeability depends on the ice or hydrate saturation and/or both in case of permafrost (ice) hydrate bearing rocks, the information provided in Section 3.2.2 should be modified to prove that the ice and hydrate bearing sediments are not barriers to the fluids.

Thanks for your comment. First, I made a slight mistake with the title of section 3.2.2. The title of this section should be “The study of the filtration properties of ice bearing rocks”, since the consideration of hydrate-containing rocks is given in section 3.2.3.

Secondly, as you correctly noted, the permeability of sediments depends on the saturation of the pore space with ice, hydrate, and unfrozen water.

This is what is emphasized in section 3.2.2, since the rocks used in the research did not have 100% saturation of the pore space and therefore were permeable. For some deposits, the water filtration coefficient was determined at temperatures of about -0.4 °C, which is close to thawing temperatures and the presence of a significant amount of unfrozen water through which filtration is possible. Filtration of hydrocarbon liquids in frozen rocks is also considered, for example diesel, the freezing point of which is significantly below 0 °C. Section 3.2.3 provides an overview of the work on gas filtration in hydrate-containing rocks. And it is also noted that such rocks have permeability when their pore space is not completely filled. And as the pore space is filled with hydrate, the permeability of the deposit can significantly decrease to the point that the rock becomes non-permeable. So sections 3.2.2. and 3.2.3 confirm that frozen and hydrate-containing rocks are not absolute fluid-resistant. Much depends on the saturation of the pore space and the greater the hydrate saturation and ice saturation, the less permeable the deposits will be, as a rule.

15. Lines 4-5 in the 2nd paragraph (Page No. 104), “the difference between the pore ice formation and hydrate formation”, should be elaborated with proper justification.

Thank you for this comment. This paragraph provides a conclusion based on the literature review presented in section 3.1. At the end of Chapter 3, I have added some clarifications:

It is also possible to form hydrates at the gas-ice boundary, at subzero temperatures, which, for example, are typical for Arctic regions. At the same time, ice is formed only from water in the pore space of rocks. And as a rule, its formation begins from soil particles, and not from the center of the pore. For the formation of ice, it is not necessary to maintain high pressures characteristic of achieving equilibrium conditions of hydrate formation. This is the main difference between hydrate formation and ice in the pore space, since ice only cements particles and fills the entire pore as the pore moisture freezes and hydrate can form in the central part of the pore at a distance from the soil particles, forming a floating structure.

16. The captions for the Figures 18a & 18b are interchanged. Please check and rectify.

Thank you for this comment. I checked this Figure. Everything is marked correctly in this figure. First, there is a diagram of the core holder (18a), and then a part of the disassembled core holder with a rubber cuff (18 b).

17. In the general schematic of the sample holder (Figure 19b), where are the temperature sensors and the set up for the acoustic measurements? Define DM?

DM is a gas pressure sensor. The text of the dissertation defines DM: “The DM sensor shows the differential pressure. The volume of gas....”.

Figure 19a shows the core holder in detail. This is the same core holder as in Fig. 19b. The temperature sensor T1 is located on the end side of the sample (next to the acoustic sensor A2). In addition, another sensor was additionally used to control the temperature, located on the core holder body and not reflected in the diagram.

18. Subsection 4.2, Page No. 110, it is mentioned that the natural sediments have been taken from permafrost horizons of north of western Siberia. However, the locations of the samples Sand 2 and Polymyrenal loam are different. Please clarify.

I have checked this information. That's right, these deposits were selected from two sites on the Yamal Peninsula from frozen rock horizons. The distance between the sampling sites on the peninsula is about 400 km and the Yamal Peninsula is completely located in the northern part of western Siberia

19. What is the meaning of letters used for Genesis Age in Table 12?

The paragraph under table 12 gives a detailed description of the soils used and a decoding of the symbols of age and genesis according to the geochronological scale: Late Jurassic age of marine genesis (mJ3), Quaternary age (Pleistocene) of marine genesis (mQ3), Paleogene deposits of marine genesis (mP1-2), Oglanlin formation of the Paleogene period of Eluvial genesis (eP2ogl), Paleogene age of eluvial genesis (eP2).

20. Plot and show the particle size distribution of all geomaterials used in the study instead of showing values in Tables 13 & 14.

Thank you for this comment. Unfortunately, I can no longer make such major changes as deleting tables and adding new drawings. Also, in all the works of the scientific group that the author belongs to (Chuvilin et al., 2018, 2020, 2021, 2022), we present the granulometric composition of the soils used in tabular form so that it can be more clearly understood which particle fraction dominates:

Chuvilin, E.M.; Grebenkin, S.I.; Zhmaev, M.V. Impact of hydrate and ice formation on gas permeability of sandy soils (Published in Russian). *Vesti Gazovoy Nauki scientific-technical collection*, 2018, 3(35), 264-273.

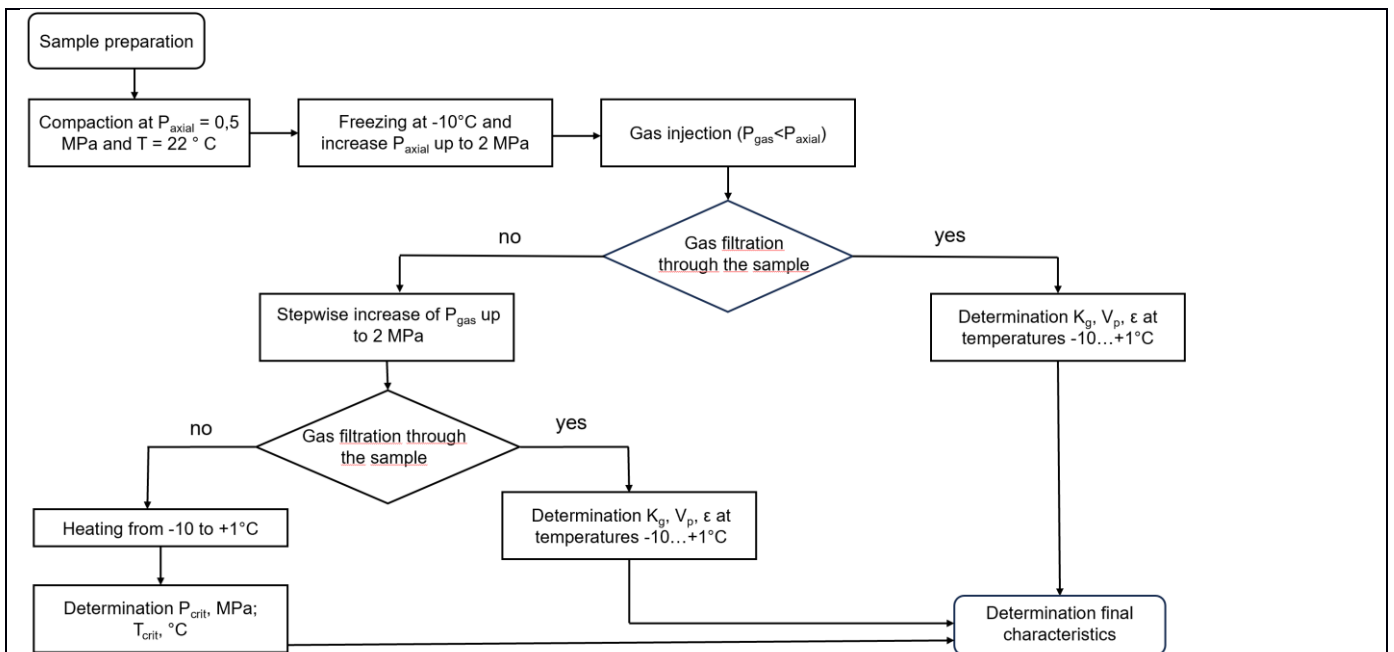
Chuvilin, E.M.; Grebenkin, S.I.; Davletshina, D.A.; Zhmaev, M.V. Influence of hydrate formation on gas permeability variations in frozen sands. *Earth's Cryosphere*, 2020, XXIV, 2, 34-40.

Chuvilin, E.; Grebenkin, S.; Zhmaev, M. Gas permeability of sandy sediments: Effects of phase changes in pore ice and gas hydrates. *Energy and Fuels*, 2021a, 35(9). <https://doi.org/10.1021/acs.energyfuels.1c00366>

Chuvilin, E.; Zhmaev, M.; Grebenkin, S. Gas permeability behavior in frozen sand controlled by formation and dissociation of pore gas hydrates. *Geosciences (Switzerland)*, 2022, 12, 9, 321.

21. Provide a flow chart for the methodology adopted for the filtration tests (Refer Subsection 4.3).

Unfortunately, I cannot add a new drawing to the text of the dissertation. However, if we consider Figure 20, then in the form of a flow chart it will look like this:



22. With reference to the sentence, “kept for 30 minutes to evenly distribute moisture in the pore space at a temperature of +22 °C (refer 115)”, how would one ensure uniform distribution of water content after 30 minutes? Clarify.

Since the sand particles are large enough and do not retain water, this method is used when preparing a soil mixture with the water content required for the experiment. In this method, the required amount of distilled water is added to an air-dry sand suspension, thoroughly mixed and left in a tightly closed container for about half an hour. After that, this mixture is loaded into the core holder in layers and a sample with evenly distributed water content is obtained. It is also worth noting that the sample after loading stands for about a day at room temperature with a small crimping pressure, which also contributes to the uniform distribution of moisture. If such a sample is frozen, removed and cut up to 1 cm, then the water content will not differ in different areas by no more than 0.1%. In this way, the sand samples presented in all our works were prepared (Chuvilin et al., 2018, 2020, 2021, 2022, 2024).

23. The cooled mixture was carefully reshaped in an airtight container, after which ice chips of no more than 1 mm in size were added to it to create the necessary humidity”, what is the significance of the necessary humidity? After that, the container was kept at room temperature (+22 °C) for an hour to evenly distribute moisture in the pore space (refer Page No: 115). How was this was achieved? Provide the photographs to justify the above statement.

Thank you for this question. I've rewritten the text a bit to make it clearer: “A thorough mixing of cooled air-dry sandy-clay soil or loam and ice chips of no more than 1 mm in size in an airtight container was carried out. Thus, the addition of ice chips made it possible to set the necessary humidity in the sample for the experiment. After that, the container with the soil mixture was kept at room temperature (+22 °C) for an hour so that the evenly distributed ice chips thawed and moisture was evenly distributed in the pore space.”

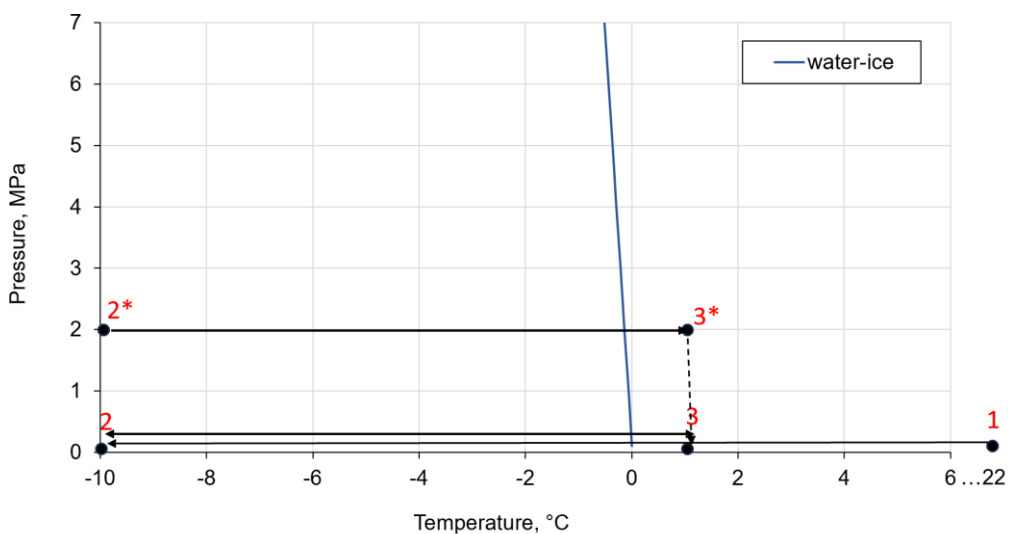
Also, throughout the text, I have replaced the term “humidity” with the term “water content”. The required water content (humidity) is necessary so that our soil corresponds to the natural water content. In experiments, water content in the range of 10-20% is usually used. After standing for a day at room temperature (+22 °C) and freezing (-5 °C), such samples have a uniform distribution of ice in the pore space and a massive cryogenic texture as in the photo:



If distilled water is simply poured into a sandy-clay soil, then it will be difficult to stir such soil, since most of the water will be unevenly connected with clay particles. And when loading such a soil mixture into the core holder, zones with heterogeneous humidity may occur in the sample.

24. Provide temperature profile for the freezing process like the profile provided for hydrates in Figure 21.

Unfortunately, I can no longer add new pictures to the text of the dissertation. I did not add this profile to the text of the dissertation, because it is not informative enough. It will look like this:



Line 1-2 is the freezing of the sample. Line 2-3 – determination of gas permeability and other properties under conditions of increasing temperature. Line 3-2 – freezing of the sample and its extraction from the core holder to determine the final characteristics.

If the sample was impermeable, then line 2-2* is an increase in gas pressure to 2 MPa, then the line 2*-3* - is the heating of the sample in order to determine the critical temperature at which a gas breakthrough will occur at a fixed pressure. Next, the sample was frozen (line 3-2) to evaluate its final properties.

25. *Provide the procedure to determine the Pcrit and Tcrit (refer Figure 20).*

In experiments with a fixed initial gas pressure, the critical temperature (Tcrit) is determined at the moment when gas filtration through the sample begins. At the same time, this initial pressure is taken as critical (Pcrit). In these experiments, the pressure is fixed, and the temperature gradually rises.

If experiments are carried out at a fixed temperature, the critical pressure will correspond to the pressure at which gas filtration begins through an initially impermeable frozen sample. In these experiments, the temperature is fixed, and the pressure gradually increases.

26. *What is the meaning of “u.f”, that appear in Page 125.*

I have added an explanation to the text starting from the first mention on page 35. u.f. is a unit fraction. For example, if we multiply 0.5 u.f. by 100%, we get 50%.

27. *In Table 20, it is mentioned that Vp table and Vs table . What does table corresponds to here? Please elaborate.*

The tabular values for the Vp and Vs from the textbook on geophysics given in table 20 are needed in order to compare them with those obtained at the experimental installation.

28. *The explanation for Figure 22 in the text is not clear and is insufficient.*

Thanks for the comment. I have added corrections to the text:

As shown in Fig.22, the difference in the velocities of primary waves (Vp) determined on the filtration unit with a geophysical module used by the author in comparison with another geophysical unit, which was calibrated on standard samples, is about 3% for ice and 1% for steel. The difference in the velocities of the secondary waves (Vs) was slightly greater and amounted to 5% for ice and about 2% for steel. In general, it can be assumed that the maximum discrepancy between the results of determining Vp and Vs is within 5% (Fig. 22).

29. *On Page no. 130, it is written, “A comparison of the results of determining Vp and Vs at two installations showed that the discrepancy between the results is within 5.2% (Fig. 5)”. Figure 5 is not relevant to this statement as it is the classification of hydrate reservoirs. Provide the justification.*

Thanks for the comment. I was wrong here, in fact it was about Figure 22.

30. *Chapter 5. Remove either ice-bearing or frozen in the heading of Subsection 5.1 (Page 132.).*

Thanks for this remark, I corrected it in the text.

31. *With reference to the Figure 23, explain the reason for the abrupt drop in pressure after 4 MPa.*

The pressure drop was recorded because during the heating of the sample, gas began to filter through it and the impermeable sample became permeable. This is noted in the text of the dissertation: “And in the experiment with a pressure drop of 4 MPa (sample SK3), the temperature of the beginning of filtration turned out to be even lower -4.6°C (Figure 23c).” Thus, for this sample, the critical temperature is -4.6°C , when a gas breakthrough occurs at a constant pressure of 4 MPa.

32. *On Page 134, it is wrongly written Figure 1a, instead of Figure 23a.*

Thanks, I fixed it.

33. *It is mentioned that the drop of pressure is related to a sharp activation of filtration in Page 134. However, it might be due to the partial melting of ice due to high pressures. Author must clarify.*

As shown in Fig. 21, with an increase in gas pressure, the water-ice phase boundary shifts to the region of negative temperatures and at a pressure of 4 MPa, it will be in the region of -0.3°C . At the same time, the gas breakthrough in the SK3 sample at a pressure of 4 MPa occurred at a temperature of -4.6°C , which is significantly lower than -0.3°C and corresponds to stable ice conditions. At pressures of 1 and 2 MPa, the water-ice boundary will be in the range of $-0.1\text{...}-0.2^{\circ}\text{C}$. For samples SK1 and SK2, the critical gas breakthrough temperatures corresponded to values of -0.3°C and -0.9°C , which is also lower than the temperature of -0.2°C at which ice can begin to melt.

34. *It is observed that the “increase in temperature during the filtration experiment led to an increase in the permeability of frozen samples, but the intensity of the change in gas permeability was different” (Figures 30 & 31). However, the author should provide the reasons/ to support this.*

The explanation of this is given by the author in the text further after Figure 32: “Filtration studies have shown that the permeability of frozen soils depends primarily on their general filling of pores with ice and unfrozen water....”

In the model sandy-clay sample, montmorillonite is present in the composition, which is characterized by a higher content of unfrozen water at a negative temperature, compared with other clay components. Figure 33 shows the curves of unfrozen water for natural loam and a model sandy-clay sample. According to these data, in the considered temperature spectrum, the content of unfrozen water in a sandy-clay sample will be higher than in loam. This explains the high permeability of the sandy-clay sample, also with an increase in temperature from -10 to -1°C there will be an increase in the amount of unfrozen water and a reduction in ice. And since water occupies a smaller volume in the pores than ice, the permeability will increase.

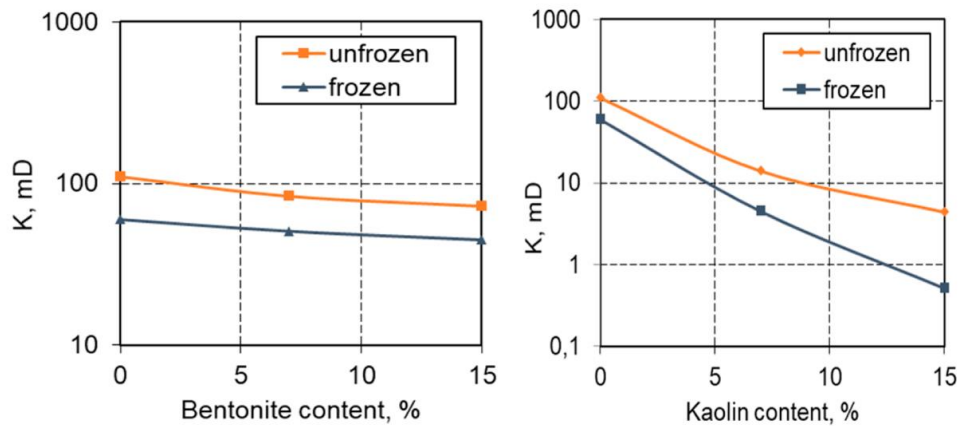
35. *The images provided in Figures 25, 26 and 27 are not clear. Please modify.*

Unfortunately, only such sample images are available. The author has tried to improve these drawings by marking areas with empty pores on them in red. A more detailed study of the structure of the samples requires more advanced equipment, such as a microscope with a cryogenic attachment.

36. *Provide a detailed explanation to understand the influence of the fine contents (clay fraction) on the gas filtration capacity during freezing and thawing of sediments.*

Similar work on the assessment of the effect of the clay component on permeability during freezing and thawing was carried out by the author during the master's thesis and was presented in the works (Chuvilin et

al., 2018; 2021). An increase in clay particles in the sand matrix leads to a decrease in gas permeability in both frozen and non-frozen sediments. At the same time, the mineral composition of clay is also important. The presence of kaolin clay affects the permeability of sand samples (both before and after freezing) more strongly than the montmorillonite component, with their percentages and initial water contents (10 %) being equal (Chuvilin et al., 2021):



The permeability decrease of sand samples containing up to 15 % of clay may vary within an order of magnitude depending on the clay mineralogy.

Chuvilin, E.M.; Grebenkin, S.I.; Zhmaev, M.V. Impact of hydrate and ice formation on gas permeability of sandy soils (Published in Russian). *Vesti Gazovoy Nauki scientific-technical collection*, 2018, 3(35), 264-273.

Chuvilin, E.; Grebenkin, S.; Zhmaev, M. Gas permeability of sandy sediments: Effects of phase changes in pore ice and gas hydrates. *Energy and Fuels*, 2021a, 35(9). <https://doi.org/10.1021/acs.energyfuels.1c00366>

37. With reference to Figure 29, substantiate increase in water content after filtration experiment.

The total moisture content of the sample before and after the experiment differed by no more than 0.1%. This graph shows the moisture analysis of half of the sample that was split lengthwise. The water content of the second half was determined entirely, without separation by 2 cm. An increase in water content towards the end of the sample is associated with purging this sample at the end of the experiment in a thawed state to assess its gas permeability at a positive temperature.

38. As per the data provided in Figure 30, it is realized that the maximum gas permeability is around 5 mD. However, the range of gas permeability 22-25 mD is used to plot the graph between Gas permeability and Temperature (refer Figure 31). Please check and clarify.

Thanks for the comment, I checked the figures. Everything is correct in these figures. Figure 30 shows the temperature dependence of permeability for samples of natural loam with different initial water content. Figure 31 shows data on permeability at different temperatures for a model sandy-clay sample.

39. With reference to the Figure 32, what is the reason for redistribution of the water content only between 6-8 cm length of the sample?

This is due to the fact that these samples, after thawing at the end of the experiment, were purged with gas (at a low gradient of about 1 bar) to assess their permeability. In view of this, a small migration of moisture to the final part of the samples is possible, which is noted in Fig. 32.

40. It has been observed that moisture and humidity are used at many places to represent the water content. What is the difference between these two and is it possible to use only one of these to eliminate the confusion.

These words are synonymous and for greater clarity, I have removed the word “humidity” and replaced it with “water content”.

41. The information provided in Figures 42, 43, 44 and 45 is not well documented.

I will try to give a brief comment on this part.

These were the first steps in the application of tomography to characterize frozen samples at this facility. Therefore, this experience is largely methodical and at this stage the author tried to describe the changes in the samples before and after filtration experiments. Often the samples were quite homogeneous (fig. 42), and it was possible to emphasize only small ice layers with a thickness of about 0.1 mm, which apparently do not affect permeability, as shown in Fig. 43. In Fig. 44a the author managed to emphasize the presence of small ice inclusions in a frozen loam sample before the start of filtration tests and their reduction at a temperature close to the thawing of this soil (Fig. 44b). This reduction occurred due to the transition of ice into unfrozen water.

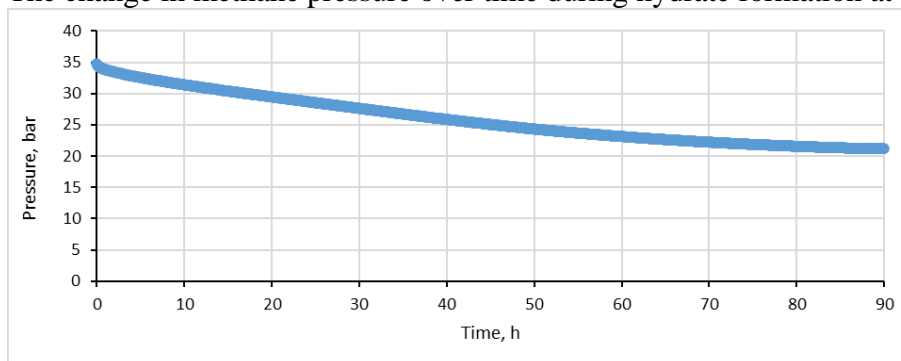
There were no visually noticeable ice inclusions in the samples, which is emphasized by figures 42a, 44c, 45.

42. Provide details (profiles of temperature and pressure) of the synthesis and dissociation of gas hydrates.

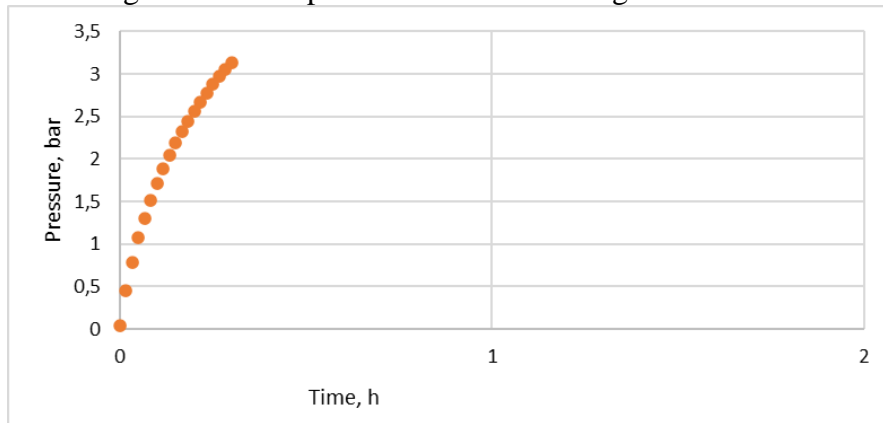
In most cases, hydrate formation was carried out at a constant temperature of -5°C . In the case of thermal cycling, temperature changes were emphasized, as for example in Fig. 48a.

Unfortunately, I cannot add graphs of pressure changes to the text of the dissertation, but I will demonstrate an example of pressure changes during hydrate formation and dissociation at -5°C .

The change in methane pressure over time during hydrate formation at -5°C .



The change in methane pressure over time during dissociation at -5°C .



43. *In Figure 47, What are the characteristics of sample TS2?*

I have made additional clarifications to the text:

... same sandy sample (TS2), which was prepared from sand 2, but with a higher degree of pore filling with ice and hydrate (68.7%). The water content of this sample was 10%. (Chuvilin et al., 2021a). This sample (TS-2) was characterized by a low permeability of 0.03 m before the dissociation stage of the pore hydrate.

44. *What is non-equilibrium pressure, mentioned in Figure 47.*

In this case, an atmospheric pressure of 0.1 MPa was meant, which would be lower than equilibrium for methane hydrate.

45. *Plot the variation in velocities with change in gas permeability during dissociation.*

When the hydrate dissociated at a negative temperature, the velocities of the longitudinal waves practically did not change, so the author did not give this graph.

46. *Explain the reason for the nonlinear behavior of gas permeability with axial pressure during unloading (Refer Figure 53).*

Thank you for this important question. Apparently, at the initial stage, after removing the load and slightly expanding the sample, due to structural and textural transformations, some filtration channels were opened or unblocked. However, in the future, with a stepwise decrease in load, gas permeability decreased quite slightly and was almost linear at 6-4 MPa, which may be due to the activation of visco-plastic deformations of ice in the pore and their attenuation. However, these statements require comprehensive studies using microtomography to analyze changes in the internal structure of samples at each stage of compaction-unloading. In the future, the author will try to implement this approach in his further work in this direction.

47. *With reference to the sentence, "In experiments with flue gas injection, the presence of nitrogen contributes to a more active decomposition of methane hydrates, which affects the increase in gas permeability at the initial stages of replacement" on Page no. 191, explain the reason for more decomposition of methane hydrates due to the presence of nitrogen.*

When nitrogen is introduced, it competes with methane for inclusion in the hydrate structure:

1)Destabilization Effect: Nitrogen molecules, being smaller and having different interaction properties compared to methane, do not stabilize the hydrate lattice as effectively. As a result, the hydrate structure becomes thermodynamically less stable.

2)Driving Force for Methane Release: The presence of nitrogen shifts the equilibrium conditions, encouraging the release of methane from the hydrate to restore equilibrium.

48. *Provide a detailed experimental methodology for conducting CH₄-CO₂ replacement in Subsection 6.3.*

Thank you for this question. The methodology for these experiments is described in detail in section 4.3.2. I also added information on the selection of the flue mixture and pressures:

In these experiments, a flue gas mixture consisting of 55%CO₂ and 45%N₂ was selected because it allowed working with a gas pressure of 4 MPa for the stable existence of CO₂ hydrates at +1 ° C. A decrease in the concentration of CO₂ and an increase in N₂ in the flue mixture leads to an increase in gas pressure, which is supplied to the core holder in order for CO₂ hydrate to exist. At the same time, the risk of gas leaks from under the rubber cuff into the hydraulic system increases, which leads to the shutdown of the experiment and long-term cleaning of the equipment. In this regard, mixtures with a high nitrogen content requiring high gas pressures were not used in these experiments.

49. Which method has been employed for hydrate synthesis?

In all experiments, author used the excess gas method to form hydrate

50. What is the influence of the dissociated water on the effective gas permeability during the dissociation process?

If water is formed during the decomposition of the hydrate, which, for example, is characteristic of dissociation at low positive temperatures, then an increase in its amount may lead to an increase in the permeability of samples, since it occupies a smaller volume in the pores compared to hydrate.

However, if there are some axial pressures on the sample, the permeability may decrease, since the presence of hydrate increases the strength properties of the sample, and when it decomposes and water accumulates, the sample may deform and its porosity decrease, which will lead to a decrease in permeability.

51. What are the “capacity properties of rocks”?

In Russia, the term “filtration-capacitance properties (or filtration and capacity properties) of rocks” is often used, which implies their permeability, porosity, and saturation of the pore space with the corresponding fluid (water, ice, hydrate, oil and etc.).

Response to Prof. Ivan Kulakov

I am grateful to Professor Ivan Kulakov for a very positive review of my PhD thesis. Although there were no specific questions and suggestions for improvement, I will be ready to answer all questions that arise during the defense.