UDC 622.279.97
DOI 10.52171/herald258

Study of Factors Affecting the Formation of Crystalline Hydrates in Gas Transportation

A.N. Gurbanov, I.Z. Sardarova, J.R. Aliyev
Azerbaijan State Oil and Industry University (Baku, Azerbaijan)

For correspondence:
Gurbanov Abdulaga / e-mail: qabdulaga@mail.ru

Abstract

In this article, changing the concentration of NaCl in solution affects the rate of hydrate formation only slightly. However, a further increase in the NaCl content in the solution reduces the rate of hydrate formation by 25%. In aqueous solutions with low concentrations of alcohols, the formation of mixed air and chloroform hydrate and propane hydrate is accelerated. It has been established that in the presence of small additions of alcohols, the mechanism of hydrate growth is similar to that observed for the growth of hydrates with the addition of surfactants. This effect manifests itself at the stage of mass crystallization. The process of hydrate formation is exothermic, therefore, to increase the rate of hydrate formation, it is necessary to intensively remove heat from the gas-water system. In experiments conducted under static conditions, this excess was about 0.3 MPa.

Keywords: gas hydrates, temperature of water, formation, transition, methanol, experiment, system.

Submitted *3 May 2024*
Published *23 June 2025*

For citation:
A.N. Gurbanov, I.Z. Sardarova, J.R. Aliyev
[Study of Factors Affecting the Formation of Crystalline Hydrates in Gas Transportation]
Herald of the Azerbaijan Engineering Academy, 2025, vol. 17 (2), pp. 35-44

Qazların nəqlində kristal hidratların əmələ gəlməsinə təsir edən amillərin tədqiqi

Ə.N. Qurbanov , İ.Z. Sərdarova, C.R. Əliyev
Azərbaycan Dövlət Neft və Sənaye Universiteti (Bakı, Azərbaycan)

Xülasə

Məqalədə kristal hidratların əmələ gəlməsinə təsir edən amillər tədqiq edilib. Məhlulda NaCl konsentrasiyasının dəyişdirilməsi hidrat əmələ gəlmə sürətinə yalnız bir qədər təsir edir. Bununla belə, məhlulda NaCl tərkibinin daha da artması hidrat əmələ gəlmə sürətini 25% azaldır. Alkoqolların az konsentrasiyası olan sulu məhlullarda qarışıq hava və xloroform hidrat və propan hidratın əmələ gəlməsi sürətlənir. Müəyyən edilmişdir ki, spirtlərin kiçik əlavələri olduqda hidratların böyümə mexanizmi səthi aktiv maddələrin əlavə edilməsi ilə hidratların böyüməsi üçün müşahidə olunana bənzəyir. Bu təsir kütləvi kristallaşma mərhələsində özünü göstərir. Hidrat əmələ gəlməsi prosesi ekzotermikdir, buna görə hidratın əmələ gəlməsi sürətini artırmaq üçün qaz-su sistemindən istiliyi intensiv şəkildə çıxarmaq lazımdır. Statik şəraitdə aparılan təcrübələrdə bu artıqlıq təxminən 0,3 MPa təşkil etmişdir.

Açar sözlər: qaz hidratları, suyun temperaturu, əmələ gəlməsi, keçidi, metanol, təcrübə, sistem.

Исследование факторов на образование кристаллогидратов при транспортировке газов

А.Н. Гурбанов, И.З. Сардарова, Д.Р. Алиев
Азербайджанский государственный университет нефти и промышленности (Баку, Азербайджан)

Аннотация

В статье, рассматриваются факторы, влияющие на образование кристаллогидратов. Изменение концентрации NaCl в растворе незначительно влияет на скорость гидратообразования. Однако дальнейшее увеличение содержания NaCl в растворе снижает скорость гидратообразования на 25%. В водных растворах с низкой концентрацией спиртов ускоряется образование смешанного воздухо-хлороформ-гидрата и гидрата пропана. Установлено, что механизм роста гидратов в присутствии небольших добавок спиртов аналогичен тому, который наблюдается при росте гидратов с добавкой ПАВ. Этот эффект проявляется на этапе массовой кристаллизации. Процесс гидратообразования является экзотермическим, поэтому для увеличения скорости гидратообразования необходимо интенсивно отводить тепло из системы «газ – вода». В экспериментах, проведенных в статических условиях, это превышение составило около 0,3 МПа.

Ключевые слова: газовые гидраты, температура воды, образование, переход, метанол, эксперимент, система.

Introduction

In the systems of production, collection, treatment, transport and processing of hydrocarbons, under certain thermobaric conditions, the formation of gas crystalline hydrates occurs, which adversely affect the operation of process equipment. To prevent and combat crystalline hydrates, it is necessary to know the time and rate of their growth.

Of all the issues related to the study of gas hydrates, the question of the kinetics of hydrate formation is the most complex. During the extraction, collection, preparation, transport and processing of hydrocarbons under certain thermobaric conditions, the formation of gas crystalline hydrates occurs, which affect the operation of process equipment.

With the study of gas hydrates, the question of the kinetics of hydrate formation is the most difficult. Affecting the speed of the hydrate formation process, the solution of which will allow the development of new technological methods for the prevention and control of crystalline hydrates.

The study of factors affecting the rate of hydrate formation is an important task, the solution of which will allow developing new and modernizing existing technological methods for the prevention and control of crystalline hydrates. The main factors are presented below.

Materials and methods

Eliminating the causes of the formation of crystalline hydrates is one of the important issues in order to prevent the failure of technological equipment used in the processing of hydrocarbon raw materials and preparing them for transportation. The important role of changes in thermodynamic parameters in the formation of crystalline hydrates has been studied. The process of gas transition into the hydrate phase until it is completely saturated in time is exponential in nature.

In the experiment, the mass concentration of propane in the gas hydrate was the maximum possible. As a result, the conditions for the penetration of gas molecules into a finely dispersed liquid are maintained at low temperatures.

Eliminating the difficulties in the preparation of natural and oil gases for transportation is one of the most urgent problems in modern times. Certain methods have been developed to prevent them. Experiments were conducted under certain conditions to prepare gases for transport and results were obtained. Hydrate formation in temperature and pressure changes, the effect of different absorbents at certain temperatures, the dynamics of hydrate formation were investigated experimentally.

The effects of water droplets in gases on hydrate freezing and activators added to gases on hydrate formation were determined under experimental conditions. The effect of the turbulization system on hydrate formation during the movement of gases in the pipelines, the effect of heat transfer and physical fields during the transportation of gases were experimentally investigated and analyzed.

The processes of formation of crystalline hydrates due to changes in pressure at certain temperatures are graphically shown. The ratio of the mass of crystalline hydrates with a change in temperature depending on the volume has been determined.

Temperature and pressure. The effect of water content of carbohydrates on hydration was investigated and the results have been graphed. In this case, the quantities of inhibitors used have been studied in a comparative manner. The changes that occur when certain salts are used as inhibitors have been studied.

The growth rate of hydrates depends on the degree of supersaturation ΔP and the thermometer force ΔT or the degree of supercooling, respectively, the difference in pressure and temperature of the medium in which the process of hydrate formation occurs, and their equilibrium values increases. However, it is noted that a high hydrate growth rate leads to a smaller filling of with an increase in ΔT, other things being equal, the growth rate of hydrates the crystal cavities with gas and to a lower stability of the resulting hydrate [1].

The stability of the hydrate depends on ΔP. The stability of a hydrate refers to the pressure of its dissociation at t ≈ 0°C. At the same ΔT, the growth rate of hydrates of the KS-I structure is more than 5 times higher than the growth rate of hydrates of the KS-II structure [2].

Fig. 1 shows the growth kinetics of natural gas and ethylene hydrates at a temperature of 278 K. During the film growth of hydrate on the free surface of water, with an increase in ΔT, an extremum of the growth rate of methane and ethane gas hydrates is observed) [3] (Fig. 2).

With an increase in the cooling rate of the system, the initial temperature of hydrate growth decreases [3]. For example, for a propane-butane mixture at p = 1.01 MPa and a cooling rate of 1K/h, the temperature of hydrate formation is -275.1K, at 5K/h -274.6K (0.5K less).

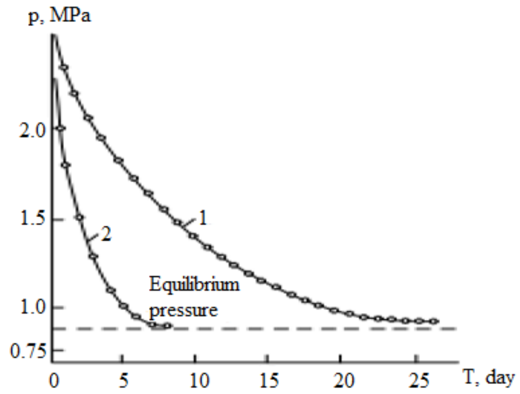
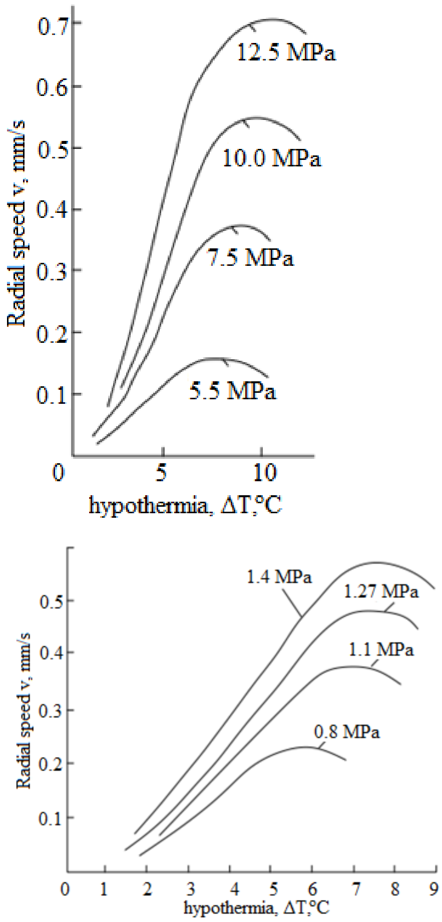


Figure 1 – Growth kinetics of natural gas and ethylene hydrates at a temperature of 278K:
1 - natural gas structure KS-II; 2-ethylene structure KS-I



a b

Figure 2 – Dependence of the radial growth rate of the surface-film hydrate of methane: *a* – and ethane; *b* – on the degree of supercooling and pressure (the numbers on the lines are the pressure of the process)

The process of gas transition to the hydrate phase until it is completely saturated in time has an exponential character, for example, as shown in the graphs (Fig. 3) for natural gas and for propane (Fig. 4).

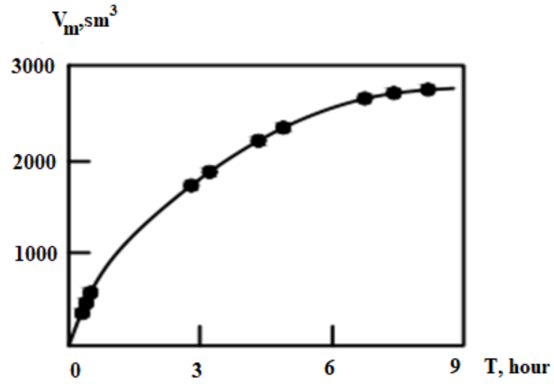


Figure 3 – Dynamics of transition of natural gas to the hydrate phase

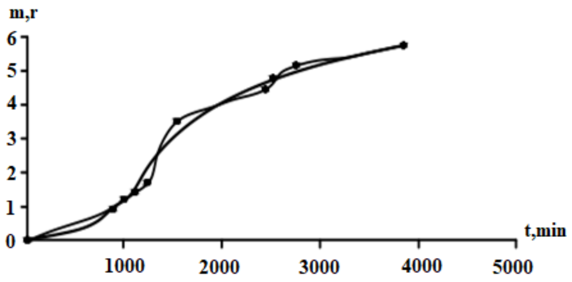


Figure 4 – Mass of propane, not affecting the lips

A decrease in the process temperature and an increase in pressure lead to an increase in the rate of hydrate formation. A decrease in temperature with an increase in pressure increases the rate of hydrate formation to a certain value, after which the rate remains constant for example, at temperatures of the order of 271–275K, an increase in pressure has little effect on the rate of gas transition to the hydrate phase. Experimental conditions: p = 0.15...0.4 MPa, T = 264...274K. In the experiment, after 60 h, the mass concentration of propane in the gas hydrate was 0.08, i.e. 56% of the maximum possible. Points of experiment [3]. The trend line is made by the authors of this article.

Water dispersion. The rate of growth of hydrates is affected by the dispersion of water in the gas-liquid system.

It is known that when the radius of water droplets decreases to micron sizes, their freezing does not occur at 0°C, but shifts to the negative temperature range. So, for example, for particles with a diameter of 1.5…2.5 µm, the freezing temperature is –35…-22°C, respectively [4]. Ice formation occurs faster from larger water particles than from smaller ones. The diffusion coefficient of gases in ice is much lower than in liquid. As a result, the conditions for the penetration of gas molecules into a finely dispersed liquid are preserved at low temperatures, i.e. at a high degree of supercooling ΔT, which causes a high growth rate of the hydrate. The smaller the particle size of water, the higher the growth rate of hydrates. Fig. 5 shows the dependence of the mole fraction of hydrate formation from a mixture of propane-butane and ice (water) particles on time.

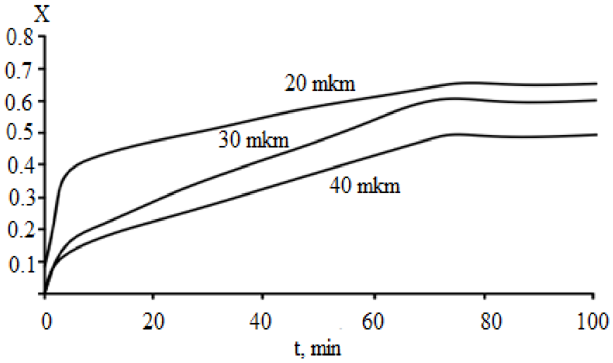


Figure 5 – Dependence of the mole fraction x of hydrate formation from propane-butane mixture (60% propane, 40% butane) and ice particles (size 20…40 µm) on time t.

Solutions and analyses. With an increase in the gas concentration in aqueous solutions, the growth rate of hydrates increases [5, 6].

The presence of salts in aqueous solutions usually reduces the rate of formation and growth of hydrates. The change in the concentration of NaCl in the solution in the range of 2 ... 6% wt. influences the rate of hydrate formation insignificantly. However, a further increase in the content of NaCl in solution reduces only 0.08 mol%. reduces the rate of hydrate formation by 25%. In this case, the resulting hydrate does not contain salts. It is noted that in the process of hydrate formation, salts accumulate in an aqueous solution. From saline solutions, the rate of formation of propane hydrates is 15 times less than the rate of formation of freon-12 hydrate ($CF_2Cl_2 \cdot 16.63H_2O$). In this case, the sizes of the resulting crystals of propane hydrates are 6 ... 30 microns, and freon -12 ≈120 microns. This effect is applied, for example, to water desalination.

The presence of aliphatic alcohols (methyl, ethyl, n-propyl, glycols) in solutions with water inhibits the formation and growth of hydrates. However, the pressure of a small amount of alcohol in the range of 1 ... 2% mol. It leads to an increase in the growth rate of hydrates (Fig. 6, 7).

With a further increase in the concentration of alcohol in the solution, the rate drops sharply [6, 7].

In aqueous solutions with a low concentration of alcohols (methyl, ethyl, n-propyl), the formation of a mixed hydrate of air and chloroform and propane hydrate is accelerated shows the kinetic curves characterizing the change in the gas content in the mixed chloroform and air hydrate at different methanol contents of 0 ... 4.21 mol [7].

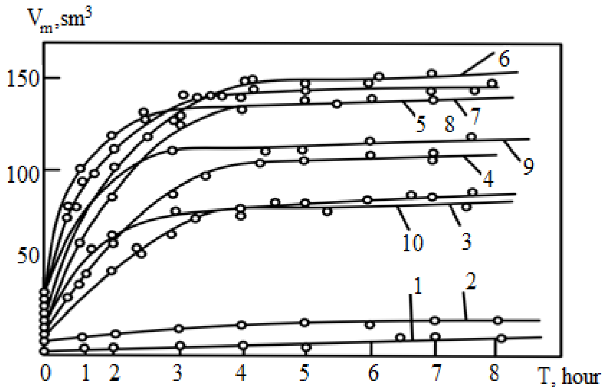


Figure 6 – Kinetic curves of changes in the gas content in the mixed hydrate of chloroform and air in the presence of methanol and without it (experimental conditions: T=263.1; p=0.1013 MPa);
1 - without methanol; 2 - 0.58% mol. methanol; 3 - 1.16%; 4 - 1.44%; 5 - 1.85%; 6 - 2%; 7 - 2.28%; 8 - 2.5%; 9 - 3.39%; 10 - 4.21%.

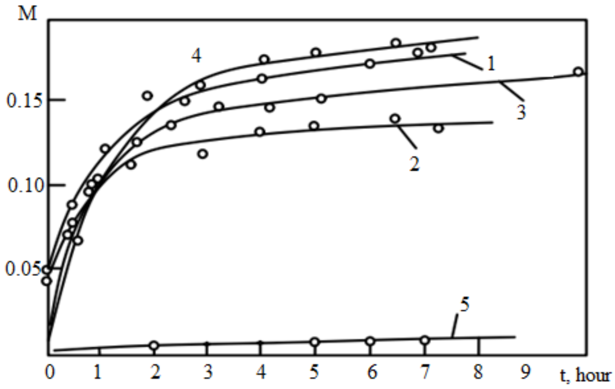


Figure 7 – The change in the gas content in the mixed hydrate of chloroform and air over time in the presence of lower alcohols: M is the number of moles of gas per 17 moles of water; 1 - methanol; 2 - ethanol; 3 - n-propanol; 4 - i-propanol; 5 - in the absence of alcohol

On shows the kinetic curves obtained for the same mixed hydrate in the presence of various alcohols [8]. To accelerate the formation of mixed hydrates, ethylene glycol was used in the CH_4+C_3H_8+ H_2O systems (at T ≈270.1 K); N_2 and O_2 [9]; chloroform with a number of auxiliary gases.

To explain the results of experiments (carried out at T<273.1 K) with different amounts of alcohols, the “isochron” method was proposed [9]. Isochrones are lines of constant time during which gas accumulates in a hydrate. The isochron method is based on measuring the amount of gas in the hydrate formed in the presence of different amounts of the added activator - alcohol for the same time (at P and T = const). For example, shows isochrones characterizing the effect of methanol in the initial solution, the content of propane bound in the hydrate has a maximum, and with an increase in the time of hydrate formation, the value of the extremum increases. The descending branches of the isochrones practically merge with each other after 4 h.

The activating effect of alcohols on the kinetics of hydrates is associated with a change in the mechanism of their growth, and not with an increase in the solubility of a gas in a liquid. It has been established that in the presence of small additions of alcohols, the hydrate growth mechanism is similar to that observed for the growth of hydrates with the addition of surfactants (surfactants) of the order of 0.05–1.0 g/l. This effect manifests itself at the stage of mass crystallization. In this case, the rate of hydrate formation increases hundreds of times. The mechanism of this phenomenon is that in the presence of surfactants, porous hydrates with a developed interfacial capillary surface are formed. The liquid under the action of capillary forces diffuses into the hydrate and intensifies its growth.

The kinetics of hydrate formation has an activating effect of an emulsifier, for example, sodium dodecyl benzenesulfonate in an amount of 0.5 ... 2.0 mol%. [9].

Turbulence of the system. Here, turbulence refers to a number of mechanical effects on the hydroforming system: mixing, gas bubbling through the liquid, oscillatory processes (for example, shaking).

Mixing of the hydrate-forming-water system intensifies the growth of hydrates (Fig. 8). An increase in the growth rate occurs due to the renewal of the hydrate-forming-water contact surface and intensive heat removal from the forming hydrates. Intensive mixing of the suspension increases the rate of hydrate formation even in aqueous NaCl solutions [9], while the inhibitory properties of the brine solution deteriorate significantly.

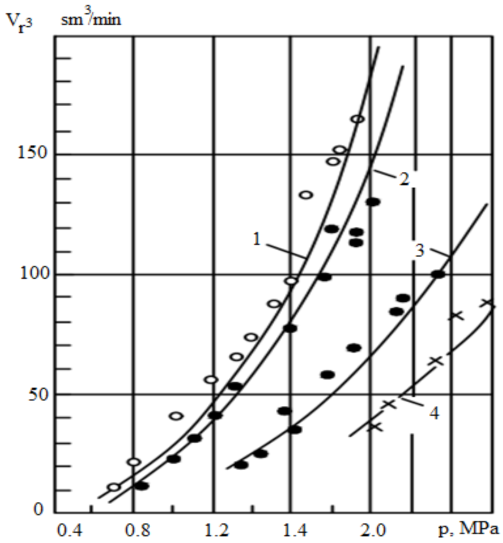
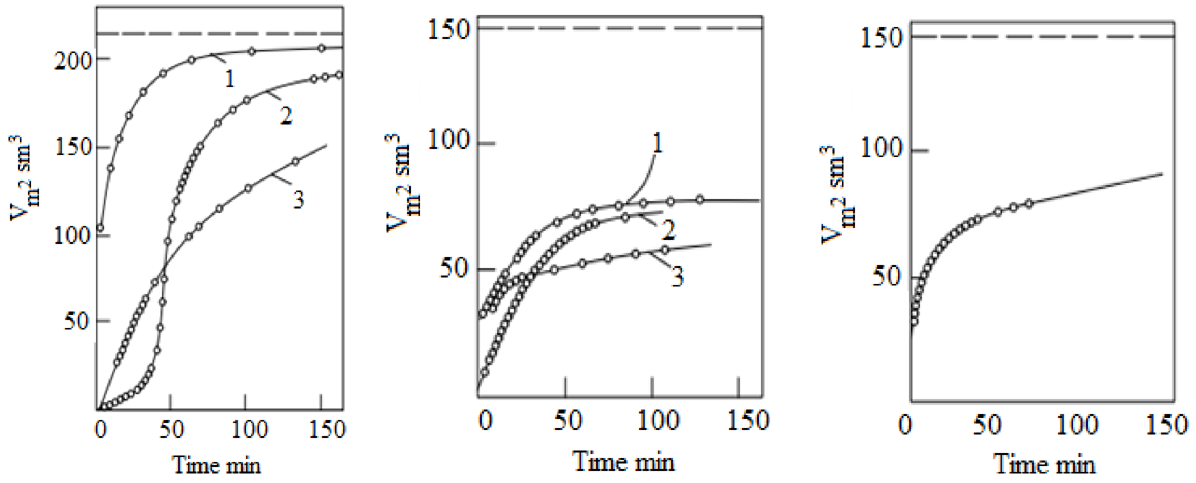


Figure 8 – Dependence of experimental at 500 rpm (points) and calculated (curves) rates of C_2H_6 hydrate formation on pressure and temperature T, K: 1 - 274.9; 2 - 275.9; 3 - 279.9; 4 - 282.3.

With intensive shaking in a gaseous medium of ice crystals with metal balls (T < 273.1 K) the formation and growth of hydrates of the CS I and CS II structures are accelerated (Fig. 9). When shaken, the hydrate crust on the surface of ice crystals is destroyed and the conditions for mass transfer are improved.



a) *b)* *c)*

Figure 9 – The rate of formation of hydrates of structures KS-I and KS-II: *a)* – reaction rate of Xe, Kr, Ar with ice crystals: 1 - Xe at p=13.2kPa and T=223.1K; 2Kr- at p= 86.7 kPa and T=190.9 K; 3-Ar at p=40 Kpa and T-90.1K; *b)* – reaction rate of Xe, Kr, Ar with a mixture of ice crystals and chloroform: 1-Xe at p=26.7 kPa and T=263.1 K; 2- Kr at p=28.0 kPa and T=195.1 K; 3 - Ar at p=48.3 kPa and T= 185.1 K; *c)* – reaction of Kr with chloroform hydrate at p=40.3 kPa and T=195.1 K; Vgas is the amount of gas absorbed by 1 g of ice

The horizontal dotted lines correspond to 10.0% filling of all cavities of the hydrate crystal lattice. The process is accelerated by bubbling auxiliary gas through a system of water and liquefied C_3-C_4 hydrocarbons [10]. In this case, the auxiliary gas bubbles mix the system and act as crystallization centers.

Heat transfer. The process of hydrate formation is exothermic, therefore, to increase the rate of hydrate formation from the gas-water system, it is necessary to intensively remove heat. The technical design of this problem is carried out mainly in two ways.

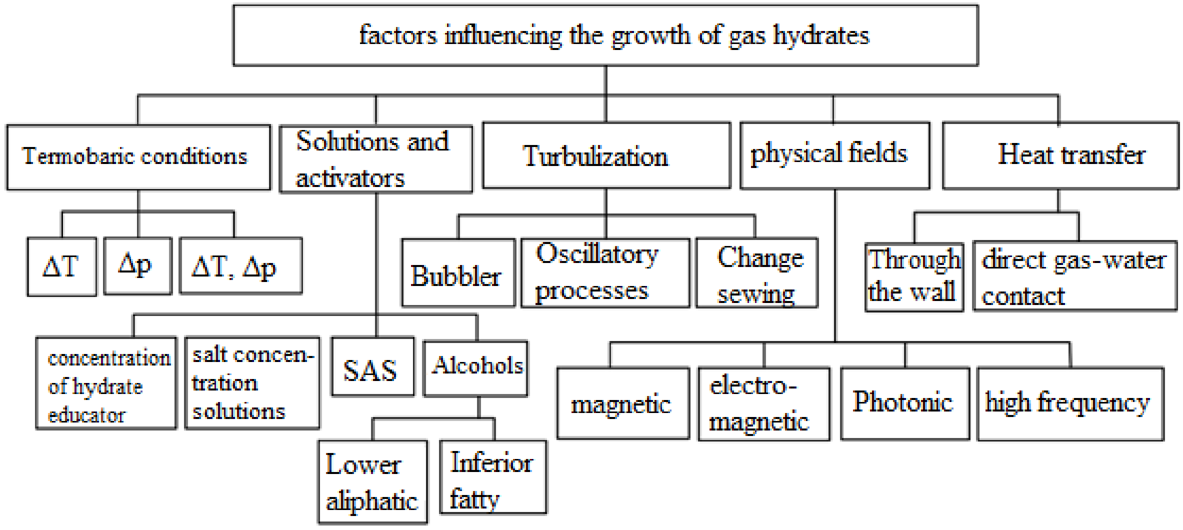
In the first, heat is removed through the wall. This method is implemented in surface-type heat exchangers. In the second method, heat is removed by direct contact of water with gas.

Physical fields. It was found that in a sample of distilled water, which was previously in a magnetic field with a strength of 2.3·105 A/m for 3.47s, hydrates formed at a temperature 1°C lower than in the control sample of water, not subjected to a magnetic field. However, the process of hydrate accumulation is significantly accelerated under the influence of magnetic fields. Static electromagnetic fields accelerate the growth of hydrates. Qualitative studies of the influence of electromagnetic fields on the formation of gas hydrates have shown that under these conditions denser and more stable crystalline hydrates are formed. The field strength, which significantly affects the equilibrium in the system, is -103 V/m.

A high-frequency electric field affects the thermobaric conditions for the formation and dissociation of crystalline hydrates. Under the necessary thermodynamic conditions in the absence of a field, the appearance of nuclei of hydrate crystals began after 30–45 minutes. In the presence of an external field, hydrate growth began after 2–3 hours. Comparison of the dissociation pressures of gas hydrates formed in the field and without the field showed that the presence of the field at a constant temperature leads to an increase in the dissociation pressure. In experiments carried out under static conditions, this excess was about 0.3 MPa at a potential difference of 2.5 kV. Daylight has an accelerating effect on the formation and growth of hydrates. During long-term observation of the development of crystals for several days at different illumination (day and night), their uneven cyclically repeating growth was noted. The cyclicity was determined by the change in the illumination of the crystals within 1 day.

Experimental conditions: fresh water, natural gas (94.2% CH_4, 3.5% C_2H_6, 1.3% C_3H_8, 0.5% C_4H_{10}, 0.2% N_2, 0.3% CO_2) p = 9.6 MPa; T=274.05K. As can be seen from the brief review, there are quite a lot of influences on the growth of hydrates. The authors made an attempt to systematize the factors considered in the review, and Tab. shows their classification scheme.

Table – Classification of the main factors affecting the growth rate of hydrates of natural and petroleum gases



Conclusions

It was determined that increasing the cooling rate of the system decreases the initial temperature of hydrate growth. When the radius of water drops is reduced to a few microns, their freezing does not occur at 0°C, on the contrary, it moves to the negative temperature region. Ice formation occurs faster in relatively larger water particles. The isochronous method is based on measuring the amount of gas hydrate formed by simultaneously adding different amounts of activating alcohol. In this case, as the time of hydrate formation increases, the extremum value increases. Descending branches of isochores practically merge after 4 hours, facilitating the preparation of gases for transport. From the conducted experiments, it is known that the effect of different amounts of activating alcohols on the kinetics of hydrates is not related to the increase in gas solubility in liquid, but to the change in their growth mechanism. As a result, the presence of surfactants causes the formation of porous hydrates, the formation and growth of hydrates is prevented.

Comparison of the dissociation pressures of gas hydrates formed in hydrated and non-hydrated areas showed that the presence of an area at a constant temperature leads to an increase in the value of dissociation pressure. It was determined by the effect of alcohol on the kinetics of hydrates.

The discussed factors were systematized and their classification scheme was presented. There are quite a few factors that influence the growth of hydrates, as can be seen from a brief overview. Using this scheme, it becomes easier to take measures against hydrate formation during gas transportation.

Conflict of Interests

The authors declare there is no conflict of interests related to the publication of this article.

REFERENCES

1. **Gritsenko A.I., Galanin I.A., Nagaev V.B.** O teplote perekhoda pri obuzovanii gazovykh gidtarov v sisteme gaz – voda // Razrabotka i ekspluatatsiya gazogidratov i gazokondensatnykh mestorozhdeniy. – M., 2016. S. 28-32.
2. **Dobrzhanskiy V.G.** Vliyanie magnitnogo poly ana kinetiku obrazovaniya gazogidratyov //Voprosy teorii i praktiki magnitnoyobrabotki vody i vodnykh system. – M., 2014. S. 93-97.
3. **Gurbanov, A., Sardarova, I., Damirova, J., & Huseynov, I.** (2023). Adsorption device treatment of associated petroleum gas for power generation. EUREKA: Physics and Engineering, (5), 14-20.
4. **Nizayeva I.Q., Makaghon Y.F.** Vozdeystvie elektromagnitnix poley na netradisionie vidi uglevodorodnogo shrya // Geologiya i poleznie Mirovogo okeana. 2013. №3. – p.42-56.
5. **Guvbanov A.N.** Development of mathematical models for drying natural gas in preparation for transport. Herald of the Azerbaijan Engineering Academy. Vol. 6. № 2. 2014. pp. 89- 96.
6. **Skripov V. P., Koverda V. P.** Spontannaya kristallizasiya pereoxlajdennix jidkostey. – M., Nauka, 2017. – 251.
7. **Şabarov A.B., Danko M.Y., Şiroşva A.V.** Proektirovanie ustanovki uskorennogo rosta gazogidrata iz ledyannix castis mikronnogo razmera v potoke gaza // Vestnik Tym.GU. -2013. - №7. – p. 42-51.
8. **Gurbanov, A., Sardarova, I., Damirova, J.,** Analysis of Gas Preparation Processes for Improvement of Gas Transportation Technology (November 18, 2021). EUREKA: Physics and Engineering, (6), 48–56, 2021. doi: https://doi.org/10.21303/2461-4262.2021.002081.
9. **Ermolaev A.S.** Creation of a stand and study of the kinetics of hydrate formation // European researcher. – 2011, №10(13). pp. 1335-1342.
10. **Waals J.H., Platteeuw J.C.** Clathrate compounds. Adv. Chem. Phys., 2007. Vol. 3. Pp. 352- 431.