



Lei Wang ^{1,2}, Zhikang Song ^{1,2,*}, Xin Huang ³, Wenjun Xu ^{1,2} and Zhengbang Chen ^{1,2}

- ¹ School of Petroleum Engineering, Yangtze University, Jingzhou 434000, China
- ² Key Laboratory of Drilling and Production Engineering for Oil and Gas, Jingzhou 434000, China
- ³ Sinopec Petroleum Exploration and Development Research Institute, Beijing 122206, China
- Correspondence: szkyangtzeu@163.com; Tel.: +86-18056012832

Abstract: This study simulated seabed high pressure and low temperature conditions to synthesize natural gas hydrates, multi-stage depressurization mode mining hydrates as the blank group, and then carried out experimental research on the decomposition and mining efficiency of hydrates by depressurization and injection of different alcohols, inorganic salts, and different chemical agent concentrations. According to the experimental results, the chemical agent with the best decomposition efficiency is preferred; the results show that: the depressurization and injection of a certain mass concentration of chemical agents to exploit natural gas hydrate is more effective than pure depressurization to increase the instantaneous gas production rate. This is because depressurization combined with chemical injection can destroy the hydrate phase balance while effectively reducing the energy required for hydrate decomposition, thereby greatly improving the hydrate decomposition efficiency. Among them, depressurization and injection of 30% ethylene glycol has the best performance in alcohols; the decomposition efficiency is increased by 52.0%, and the mining efficiency is increased by 68.2% within 2 h. Depressurization and injection of 15% calcium chloride has the best performance in inorganic salts; the decomposition efficiency is increased by 46.3%, and the mining efficiency is increased by 61.1% within 2 h. In the actual mining process, the appropriate concentration of chemical agents should be used to avoid polluting the environment.

Keywords: natural gas hydrate; depressurization and chemical injection combined method; hydrate decomposition efficiency; hydrate recovery efficiency

1. Introduction

As a new type of strategic energy in the future, the exploitation of natural gas hydrate is of great significance. The mining principle is to change the stable phase equilibrium condition of natural gas hydrate, and decompose natural gas hydrate to obtain natural gas. The mining methods proposed by domestic and foreign hydrate mining experts mainly include the pressure reduction method, the chemical injection method, the heat injection method and the carbon dioxide replacement method [1,2]. Judging from the current indoor test research and test mining, the pressure reduction method is more preferred.

The depressurization method reduces the pressure of the hydrate reservoir to below the equilibrium pressure of the hydrate phase, and destroys the stability of the natural gas hydrate [3]. Almenningen et al. [4] considered the depressurization method to be the most cost-effective method through field examples and the status quo. However, the experimental results of Li et al. [5], Wang et al. [6], and Zhou et al. [7] show that the depressurization amplitude has a great influence on depressurization mining efficiency. Zhao et al. [8] found that excessive pressure reduction may lead to reservoir instability. Song et al. [9] simulated vertical well pressure reduction mining through ABAQUS and found that reducing production pressure can effectively increase hydrate production, but formation subsidence is also more likely to occur. Konno et al. [10] found that the excessive



Citation: Wang, L.; Song, Z.; Huang, X.; Xu, W.; Chen, Z. Study on the Influence of Pressure Reduction and Chemical Injection on Hydrate Decomposition. *Processes* **2022**, *10*, 2543. https://doi.org/10.3390/ pr10122543

Academic Editors: Ofelia de Queiroz Fernandes Araujo and Vladimir S. Arutyunov

Received: 6 October 2022 Accepted: 22 November 2022 Published: 29 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). production of a pressure difference could lead to problems such as ice plugging or secondary hydrate formation in the wellbore. The single depressurization method still faces the problems of the rapid decay of the mining rate, low heat transfer efficiency, and low energy utilization rate, but the use of stepped depressurization (i.e., multi-stage depressurization) can effectively alleviate such problems. Therefore, using only the depressurization method is not suitable for the long-term development of natural gas hydrate.

The chemical agent injection method is to inject chemical agents into the formation to move the phase equilibrium curve of natural gas hydrate to a higher pressure and lower temperature, so that the natural gas hydrate is decomposed [11,12]. The advantage of the chemical injection method is that the heat required for the decomposition of natural gas hydrate can be reduced, and the decomposition rate of natural gas hydrate can be effectively increased in a short time. Sung et al. [13], Fan et al. [14] studied the effects of the pressure reduction method and chemical injection method on the heat of hydrate decomposition, and found that the chemical injection can significantly reduce the heat required for natural gas hydrate decomposition and increase the decomposition efficiency. Sun et al. [15] found through experiments that, compared with the conventional depressurization method, ethylene glycol injection can significantly improve the recovery efficiency of natural gas hydrate. Sun et al. [16] used a small three-dimensional device to deepen the study of chemical injection to extract methane hydrate, and explored from the aspects of injection concentration and injection rate. To sum up, chemical injection can effectively make up for the shortage of depressurization mining.

In recent years, the combined depressurization and extraction technologies of natural gas hydrate mainly include the depressurization and heat injection combined method, the depressurization and replacement combined method, the depressurization and ground decomposition combined method, etc. [17]. Among them, Sun et al. [18] established a mathematical model, and the combined method of depressurization and heat injection can greatly reduce the water cut and improve the recovery factor. Li S X et al. [19] and Bai Y H et al. [20] found through physical and numerical simulations, that although the combined method of heat injection and depressurization can effectively improve energy utilization, long-term depressurization may lead to reservoir instability. Gupta et al. [21] found that the depressurization and CO₂ replacement method is efficient and economical, and can effectively solve the permeability problem, but this method must strictly limit the large amount of CO_2 overflow, so it has extremely high technical requirements and is not suitable for conventional mining. The combined method of depressurization and ground decomposition can easily cause formation instability due to the instability of shallow hydrate reservoirs on the seabed and the simultaneous action of pressure drop and shallow mining, so the mining efficiency of this method is low. However, depressurization and chemical injection can avoid the secondary formation of hydrate under the action of chemical agents [22], and greatly improve the recovery efficiency in a short period of time, obtain considerable economic benefits, and maintain reservoir stability. There are also other technologies that increase the production rate, such as asphaltene control [23].

At present, there is a serious lack of basic data on the effect of that multi-stage depressurization and chemical injection combined method on hydrate recovery efficiency. It is necessary to verify the feasibility of the multi-stage depressurization and chemical injection method through experimental simulation, and at the same time, it is necessary to evaluate the performance of efficient decomposition promotion. It can provide reasonable guidance for the efficient exploitation of natural gas hydrate.

In this paper, self-made equipment is used to simulate the temperature and pressure conditions of submarine hydrate reservoirs to generate hydrates with high saturation, and a multi-stage depressurization and chemical injection combined exploration of natural gas hydrate is carried out. The influence of the recovery efficiency, instantaneous gas production dynamics, and the cumulative gas production changes during the hydrate decomposition process were studied.

3 of 10

2. Materials and Methods

2.1. Experimental Materials and Equipment

Experimental materials: deionized water, made in the laboratory; methane gas (purity 99.99%), Wuhan Huaxin Gas Company; quartz sand (0.82 mm, porosity 0.45), Shanghai Sinopharm Reagent Chemical Factory; methanol (\geq 99%), ethylene glycol (\geq 99.5%), ethanol (\geq 95%), calcium chloride (\geq 96%), sodium chloride (\geq 99.5%), potassium chloride (\geq 99.5%), Longxi Science.

Experimental equipment: A XFH-II type natural gas hydrate synthesis and decomposition simulation device was used in the experiment. The schematic diagram of the composition of the gas hydrate synthesis and decomposition device is shown in Figure 1. The device consists of an injection system, a pressurization system, a constant temperature control system, a reactor system, a gas metering system and a data acquisition system. Among them, the high-pressure stainless steel reaction kettle has a volume of 500 mL, a pressure resistance of 20 MPa, and a working temperature of -20 to 50 °C; the temperature sensor range is greater than 400 °C, and the accuracy is 0.1 °C; the gas flow meter range is 1000 mL/min, and the accuracy is 0.1 mL/min.



Figure 1. Schematic diagram of the composition of the gas hydrate synthesis and decomposition device.

2.2. Experimental Steps

2.2.1. Natural Gas Hydrate Synthesis Steps

More than 90% of natural gas hydrates exist in seabed sediments with a temperature of 0-10 °C and a pressure of more than 10 MPa [24]. The main composition of hydrate deposits is silt in the South China Sea, with a porosity of 33% to 55% [25] and an average gas hydrate saturation of 13.7% to 45.2% [26]. Therefore, this experiment is based on the above research to ensure that the basic requirements of the natural gas hydrate reservoir environment are met. First, ensure that methane hydrate with high saturation is generated, and then ensure that the pressure in the kettle is about 10 MPa after the methane hydrate is completely generated. After many experiments and tests, when the experimental temperature is 4 °C and the initial pressure is about 15 MPa, and the quartz sand with particle size of 0.82 mm and porosity of 0.45 is selected to simulate the reservoir, basic methane hydrate reservoir conditions can be achieved.

Natural gas hydrate synthesis steps: ① Rinse the reactor with distilled water 3 times to remove other chemical reagents left in the reactor from the previous experiment; ② After connecting the pipeline, check the airtightness of the device, and inject 4 MPa of gas into the reaction kettle. If the pressure remains stable within 24 h, the airtightness is good; ③ Fill the reaction kettle with sand to 350 mL; ④ Add distilled water to predetermined mass (160 g); ⑤ Open the exhaust valve, and quickly and repeatedly replace the air in the reaction kettle with high-purity methane gas sample twice, so as to ensure that the gas in the kettle has the same composition as the prepared gas as much as possible; ⑥ Use a constant temperature water bath to adjust the temperature in the kettle to 4 °C, and in the process of waiting for the temperature to reach a constant value, prepare a decomposer solution for later use; ⑦ Methane gas was injected into the reaction kettle, and the injection of methane gas was stopped after the pressure in the kettle reached 15 MPa. When the pressure in the reactor is stable (observation for 2 h), the hydrate reaction is complete.

2.2.2. Natural Gas Hydrate Decomposition Steps

① After the hydrate is completely formed, multi-stage depressurization is carried out, the pressure in the reactor is reduced to the specified decomposition and production pressure for many times (the pressure shall be maintained after each stage of depressurization, and the mining shall be continued for 1 h), and the chemical agent solution prepared in advance is passed through the advection pump. The chemical agent solution was injected into the reactor at the injection rate of 8 mL·min–1, so that the hydrate began to decompose; ② When the gas production rate dropped to 0, the hydrate decomposition reaction was considered to be over; ③ The data acquisition system was used to record the temperature and pressure changes in the reaction kettle during the whole experiment process, save the data after the experiment was completed, and clean the reaction kettle.

3. Results

3.1. Multi-Stage Depressurization and Alcohol Injection to Promote Hydrate Decomposition

At 4 °C, the equilibrium pressure of the methane hydrate phase is 3.9 MPA [27]. In the actual production process of hydrate reservoirs, an excessive wellhead pressure difference may impact the wellbore and cause it to be damaged or collapse. Therefore, the three-stage depressurization mode of -4 MPa-3 MPa-2 MPa was used in the experiments. The use of the third-order depressurization mode can not only reduce the risk of reservoir collapse, but also shorten the effective production time of natural gas hydrate and increase the decomposition efficiency of natural gas hydrate. The mining conditions of multi-stage depressurization +20%/30% ethylene glycol, multi-stage depressurization +20%/30% ethanol were investigated respectively, and they were decomposed with pure depressurization. Methods were compared. The experiment was repeated 3 times, and a set of data closest to the average was taken. The experimental results are shown in Figures 2 and 3 and Table 1.



Figure 2. Decomposition curve of multi-stage depressurization and injection of 20% alcohol hydrate: (a) Instantaneous gas production rate; (b) Cumulative gas production.



Figure 3. Decomposition curve of multi-stage depressurization and injection of 30% alcohol hydrate: (a) Instantaneous gas production rate; (b) Cumulative gas production.

Index	Pure Multistage Buck	Multi-Stage Depressur- ization + 20% Ethylene Glycol	Multi-Stage Depressur- ization + 30% Ethylene Glycol	Multi-Stage Depressur- ization + 20% Methanol	Multi-Stage Depressur- ization + 30% Methanol	Multi-Stage Depressur- ization + 20% Ethanol	Multi-Stage Depressur- ization + 30% Ethanol
Experimental pressure/MPa	14.85	14.82	14.80	14.81	14.83	14.81	14.83
Experimental temperature/°C	4	4	4	4	4	4	4
Experiment end pressure/MPa	10.27	10.12	10.30	10.14	10.24	10.34	10.24
Hydrate Saturation/%	48.0	48.5	46.5	48.5	48.0	46.1	48.2
Injection rate/(mL·min ⁻¹)	8	8	8	8	8	8	8
Buck mode/MPa	-4-3-2	-4-3-2	-4-3-2	-4-3-2	-4-3-2	-4-3-2	-4-3-2
Cumulative gas production/L	48.83	54.51	54.14	53.25	53.47	53.76	53.45
Decomposition complete time/min	300	163	144	163	152	194	179
Average gas production rate/(mL·min ⁻¹)	161.7	334.4	376.0	326.7	351.8	277.1	298.6

Table 1. Relevant experimental parameters of gas hydrate depressurization and alcohol injection production.

It can be seen from Figures 2 and 3 and Table 1 that in the pure depressurization mode, when the pressure is reduced to 4.00 MPa for constant pressure production, the instantaneous gas production rate increases rapidly, and then decreases rapidly. This is because the decomposition occurs when the pressure is reduced to 4.00 MPa. The driving force is insufficient, the decomposition gas production is small, the instantaneous

gas production rate cannot be supported, and the gas production is basically free gas; the migration in the hydrate layer causes the decomposition of methane hydrate, and the instantaneous gas production rate is greatly improved, which is obviously better than pure depressurization production. Among them, the decomposition performance of multi-stage depressurization + 20%/30% ethylene glycol mode is the best, and the time required for multi-stage depressurization + 20% ethylene glycol and multi-stage depressurization + 30% ethylene glycol to completely decompose natural gas hydrate is 163 min and 144 min, respectively. Compared with pure multi-stage depressurization, the decomposition efficiency is increased by 45.7% and 52.0%, respectively. When multi-stage depressurization + 30% ethylene glycol is produced at a constant pressure of 4.00 MPa, the early instantaneous gas production rate exceeds 750 mL/min, the gas production rate is still 292 mL/min in the later stage, which is obviously better than other alcohols; when the multi-stage depressurization + 30% ethylene glycol is produced at a constant pressure of 3.00 MPa, the instantaneous gas production rate in the final stage drops to 78 mL/min, this is because the hydrate has basically completely decomposed during the constant pressure production of 4.00 and 3.00 MPa in the multi-stage depressurization + 30% ethylene glycol mode, and the decomposed gas is insufficient, so the instantaneous gas production rate drops rapidly.

Since the initial pressure is about 14.85 MPa, and multi-stage depressurization is reduced to 2.00 MPa, the final cumulative gas production should be basically the same within the allowable error range. In order to understand the production efficiency of the combined method in a certain period of time, the gas production at the end of production at a constant pressure of 4.00 and 3.00 MPa (i.e., 2 h of production) was selected for comparison. It can be seen from Figures 2 and 3 that the production efficiency of multi-stage depressurization and alcohol injection in the first 2 h of production time is much greater than that of the pure depressurization mode. The mining efficiency of +30% ethylene glycol is the best; compared with the pure multi-stage depressurization mode, the multi-stage depressurization +20% ethylene glycol mode increases the production efficiency by 65.3%, and the multi-stage depressurization +30% ethylene glycol mode produces Efficiency increased by 68.2%.

From the experimental results, multi-stage depressurization and alcohol injection can effectively improve the extraction and decomposition efficiency of hydrate reservoirs compared with simple depressurization. In addition, the chemical concentration of the combined method is much lower than that of Wang et al. [28], which is more efficient and economical. This is because the multi-stage depressurization destroys the stability of the hydrate, and, secondly, the organic reagents such as ethylene glycol, methanol, ethanol and other alcohol molecules, and the hydrophilic hydroxyl group destroys the crystal structure of the hydrate and promotes the decomposition of the hydrate [29]. At the same time, with the increase of alcohol concentration, the hydrate decomposition efficiency also increased gradually. This is because the high-concentration alcohol solution has a greater impact on the phase equilibrium conditions of methane hydrate, and adding highconcentration alcohol solution can reduce the decomposition heat of methane hydrate [15], which improves the decomposition efficiency of hydrate.

The experiment found that ethylene glycol had the best effect on promoting the decomposition of hydrate. This is because, compared with methanol and ethanol, the decomposition heat in ethylene glycol solution is lower, and the cluster structure formed by methanol molecules and ethanol molecules reduces the number of active molecules, which is not conducive to the decomposition of hydrates [30].

3.2. Multi-Stage Depressurization and Salt Injection to Promote Hydrate Decomposition

High-quality salts may crystallize and cause blockage of the injection pipeline. Therefore, multi-stage depressurization + 10%/15% calcium chloride, multi-stage depressurization + 10%/15% sodium chloride, multi-stage depressurization + 10%/15% potassium chloride are the best. The mining conditions of decompression + 10%/15% potassium chloride were compared with pure decompression decomposition. The experiment was repeated three times, and the group closest to the average was taken. The experimental results are shown in Figures 4 and 5 and Table 2.



Figure 4. Decomposition curve of multi-stage depressurization and injection of 10% salt hydrate: (a) Instantaneous gas production rate; (b) Cumulative gas production.



Figure 5. Decomposition curve of multi-stage depressurization and injection of 15% salt hydrate: (a) Instantaneous gas production rate; (b) Cumulative gas production.

Index	Pure Multistage Buck	Multi-Stage Depressur- ization + 10%CaCl ₂	Multi-Stage Depressur- ization + 15% CaCl ₂	Multi-Stage Depressur- ization + 10% NaCl	Multi-Stage Depressur- ization + 15% NaCl	Multi-Stage Depressur- ization + 10% KCl	Multi-Stage Depressur- ization + 15% KCl
Experimental pressure/MPa	14.85	14.92	15.07	14.91	14.86	14.85	14.86
Experimental temperature/°C	4	4	4	4	4	4	4
Experiment end pressure/MPa	10.27	10.46	10.40	10.24	10.48	9.33	10.07
Hydrate Saturation/%	48.0	46.5	48.2	49.1	45.7	57.2	50.5
Injection rate/(mL·min ⁻¹)	8	8	8	8	8	8	8
Buck mode/MPa	-4-3-2	-4-3-2	-4-3-2	-4-3-2	-4-3-2	-4-3-2	-4-3-2
Cumulative gas production/L	48.83	53.84	55.20	54.17	52.92	53.90	53.11
Decomposition complete time/min	300	174	161	211	189	289	240
Average gas production rate/(mL·min ⁻¹)	161.7	309.4	342.9	256.7	280.0	186.5	221.3

Table 2. Relevant experimental parameters of gas hydrate depressurization and salt injection production.

As can be seen from Figures 4 and 5 and Table 2, after the combined method of multistage depressurization and salt injection is adopted, the instantaneous gas production rate is also significantly improved, which is better than that of pure multi-stage depressurization; multi-stage depressurization and injection of 10% Calcium chloride, multi-stage depressurization and injection of 15% calcium chloride all show excellent decomposition performance, the instantaneous gas production rate at the constant pressure stage of 4 and 3 MPa is significantly higher than that of other salt injections as the hydrate is rapidly decomposed. Therefore, the natural gas hydrate decomposes completely at a relatively fast rate during the constant pressure decomposition of 2 MPa; the time required for the multi-stage depressurization + 10% calcium chloride injection and the multi-stage decompression + 15% calcium chloride injection to completely decompose the natural gas hydrate are, respectively, 174 min and 161 min, and the decomposition efficiency was increased by 42.0% and 46.3%, respectively compared with pure multistage depressurization.

It was found from the experimental process that the mining efficiency of multi-stage depressurization + 10% calcium chloride injection and multi-stage depressurization + 15% calcium chloride injection is high, and much larger than the pure multi-energy depressurization mode; compared with the pure multi-energy depressurization mode, the mining efficiency of multi-stage depressurization + 10% calcium chloride injection is improved by 54.6%, and the mining efficiency of multi-stage depressurization + 15%, while calcium chloride injection is improved 61.1%.

From the experimental results, multi-stage depressurization and salt injection can effectively improve the extraction and decomposition efficiency of hydrate reservoirs compared with simple depressurization, and it increases with the increase of mass concentration, which is consistent with the experimental results of Ding et al. [31]. This is due to the strong coulomb force of inorganic salt reagents, and it is easy to break the hydrate crystal structure through the combination of hydrogen bonds and water molecules, thereby promoting the decomposition of hydrates. This ability increases with the increase of particle concentration; inorganic salts can change the self-diffusion effect of water molecules in the system. As the mass concentration of inorganic salt increases, the activity of water molecules in the solution decreases and the self-diffusion coefficient decreases, while the self-diffusion coefficient of water molecules in hydrates increases [32], thereby promoting the decomposition of hydrates.

It was also found from the experiment that calcium chloride has the best effect on promoting the decomposition of natural gas hydrate. This is because the addition of salt solution reduces the energy required for hydrate decomposition; in calcium chloride solution, the energy required for natural gas hydrate decomposition is very low, and the ability to destroy the natural gas hydrate lattice is stronger [33] and more favorable for hydrate decomposition.

4. Conclusions

The experimental study found that multi-stage depressurization combined with the chemical agent injection method can increase mining efficiency by more than 68% in the first two hours after chemical agent injection, compared with the single depressurization method, which has the advantage of significantly increasing the mining efficiency. However, considering the field exploitation of natural gas hydrates, this method also has some limitations. Multi-stage depressurization combined with the injection of thermodynamic chemicals with a higher mass concentration (such as methanol, ethylene glycol, etc.) may pollute the environment and cost more.

From the perspective of economic and environmental benefits, the combined method needs to reasonably optimize the injection amount of thermodynamic chemicals or use multiple chemicals together to reduce costs and increase gas production. Secondly, in the future, it is necessary to constantly develop green, efficient, and economic kinetic chemicals to replace traditional thermodynamic chemicals. I believe that the reasonable application of multi-stage depressurization combined with chemical injection method is expected to be an efficient method for the on-site exploitation of natural gas hydrate.

Author Contributions: Conceptualization, Z.S. and L.W.; methodology, Z.S. and L.W.; software, Z.S.; validation, Z.S. and Z.C.; formal analysis, Z.S. and L.W.; investigation, Z.S. and W.X.; resources, L.W.; data curation, Z.S. and Z.C.; writing—original draft preparation, Z.S.; writing—review and editing, Z.S.; visualization, L.W.; supervision, L.W.; project administration, L.W.; funding acquisition, L.W. and X.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the project group of the Ministry of Science and Technology of Sinopec "Research on the Key Technologies of Effective Exploitation of Natural Gas Hydrate", grant number P20040-4.

Institutional Review Board Statement: The study does not involve humans or animals.

Informed Consent Statement: The study does not involve humans or animals.

Data Availability Statement: Not applicable.

Acknowledgments: Thanks to other authors for his support of the experimental methods, experimental materials and amendments to the content of the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Huang, X.; Wang, H.B.; Zhang, L.; He, J.Y.; Cen, X.Q. Research progress on production stimulation technology of natural gas hydrate reservoir exploitation. *Sci. Technol. Eng.* 2022, 22, 3405–3415.
- 2. Zhang, X.B.; Lu, X.B.; Liu, L.L. Research progress on natural gas hydrate extraction methods. Adv. Geophys. 2014, 29, 858–869.
- Collett, T.S.; Ginsburg, G.D. Gas hydrates in the Messoyakha gas field of the west Siberian basin—A re-examination of the geologic evidence. *Int. J. Offshore Polar Eng.* 1998, *8*, 22–29.
- 4. Almenningen, S.; Flatlandsmo, J.; Fernø, M.A.; Ersland, G. Production of sedimentary methane hydrates by depressurization. SPE Bergen One Day Seminar. *OnePetro* **2016**.
- Li, G.; Li, B.; Li, X.S.; Zhang, Y.; Wang, Y. Experimental and numerical studies on gas production from methane hydrate in porous media by depressurization in pilot-scale hydrate simulator. *Energy Fuels* 2012, 26, 6300–6310. [CrossRef]

- 6. Wang, Y.; Feng, J.C.; Li, X.S.; Zhang, Y.; Li, G. Analytic modeling and large-scale experimental study of mass and heat transfer during hydrate dissociation in sediment with different dissociation methods. *Energy* **2015**, *90*, 1931–1948. [CrossRef]
- 7. Zhou, Y.; Castaldi, M.J.; Yegulalp, T.M. Experimental investigation of methane gas production from methane hydrate. *Ind. Eng. Chem. Res.* 2009, *48*, 3142–3149. [CrossRef]
- Zhao, J.; Shi, D.; Zhao, Y. Mathematical model and simulation of gas hydrate reservoir decomposition by depressurization. *Oil Gas Sci. Technol.* 2012, 67, 379–385. [CrossRef]
- 9. Song, B.; He, Y.; Fan, Q.; Wu, Z.; Yang, B.; Zhou, Y. Numerical Study on Gas Production and Stratum Response to Marine Hydrate Dissociation Directed by Depressurization. In Proceedings of the 31st International Ocean and Polar Engineering Conference, Rhodes, Greece, 20 June 2021.
- 10. Konno, Y.; Jin, Y.S.; Shinjou, K.; Nagao, J. Experimental evaluation of the gas recovery factor of methane hydrate in sandy sediment. *RSC Adv.* **2014**, *4*, 51666–51675. [CrossRef]
- 11. Quan, H.P.; Li, Q.; Chen, T.D.; Ma, Q.; Zhai, X.E. Synthesis of a kinetic gas hydrate inhibitor. Sci. Technol. Eng. 2013, 13, 3986–3989.
- 12. Kawamura, T.; Sakamoto, Y.; Ohtake, M.; Yamamoto, Y.; Haneda, H.; Yoon, J.H.; Komai, T. Dissociation behavior of hydrate core sample using thermodynamic inhibitor. *Int. J. Offshore Polar Eng.* **2007**, *16*, 5–9.
- 13. Sung, W.; Kang, H. Experimental investigation of production behaviors of methane hydrate saturated in porous rock. *Energy Sources* **2003**, *25*, 845–856. [CrossRef]
- 14. Fan, S.S.; Tian, G.L.; Liang, D.Q.; Liang, D.; Li, D. Natural gas hydrate dissociation by presence of ethylene glycol. *Energy Fuels* **2006**, *20*, 324–326. [CrossRef]
- 15. Sun, Y.F. Experimental Study on Gas Hydrate Exploitation Combined with Depressurization and Other Technologies; China University of Petroleum: Beijing, China, 2019.
- 16. Sun, Y.F.; Zhong, J.R.; Li, W.Z.; Ma, Y.M.; Li, R.; Zhu, T.; Ren, L.L.; Chen, G.J.; Sun, C.Y. Methane Recovery from Hydrate-Bearing Sediments by the Combination of Ethylene Glycol Injection and Depressurization. *Energy Fuels* **2018**, *32*, 7585–7594. [CrossRef]
- 17. Zhang, J.; Guan, F.J.; Zhao, H. Feasibility analysis of natural gas hydrate exploitation by binary composite technology. *Contemp. Chem. Ind.* **2018**, *47*, 309–312.
- Sun, T.; Chen, Y.; Zhao, Y. Combining DWS Depressurization Method and Heat Injection to Improve the Hydrate Recovery. In Proceedings of the Offshore Technology Conference, Richardson, TX, USA, 30 April 2018.
- 19. Li, S.X.; Chen, Y.M.; Zhang, W.W.; Xia, X.R. Experimental study on heat injection and depressurization production of natural gas hydrate in porous media. *Exp. Mech.* **2011**, *26*, 202–208.
- 20. Bai, Y.H.; Li, Q.P. Simulation of gas hydrate reservoirs combined with warm water injection and pressure reduction method. *Sci. China Tech. Sci.* **2011**, *41*, 262–268.
- 21. Gupta, A.; Aggarwal, A. Gas hydrates extraction by swapping-depressurisation method. In Proceedings of the Offshore Technology Conference-Asia, Kuala Lumpur, Malaysia, 25 March 2014.
- 22. Wang, B.; Fan, Z.; Wang, P.F.; Liu, Y.; Zhao, J.; Song, Y. Analysis of depressurization mode on gas recovery from methane hydrate deposits and the concomitant ice generation. *Appl. Energy* **2018**, 227, 624–633. [CrossRef]
- Khormali, A.; Sharifov, A.R.; Torba, D.I. The control of asphaltene precipitation in oil wells. *Pet. Sci. Technol.* 2018, 36, 443–449. [CrossRef]
- Liu, D.J.; Qi, L.P. Research progress on formation mechanism and reserve prediction of seabed sandstone hydrate. J. Petrochem. Univ. 2021, 34, 76–84.
- 25. Wang, D.D. Geological Characteristics and Physical Properties of Low-Permeability Weakly Consolidated Hydrate Reservoirs in the South China Sea; China University of Geosciences: Wuhan, China, 2021. [CrossRef]
- 26. Dai, S.J. Study on the remodeling of gas hydrate sediment samples in the South China Sea. China Pet. Chem. Stand. Qual. 2022, 42, 129–131.
- Gayet, P.; Dicharry, C.; Marion, G.; Graciaa, A.; Lachaise, J.; Nesterov, A. Experimental determination of methane hydrate dissociation curve up to 55MPa by using a small amount of surfactant as hydrate promoter. *Chem. Eng. Sci.* 2005, 60, 5751–5758. [CrossRef]
- 28. Wang, Y.F.; Sun, C.Y.; Yu, X.C.; Wang Qing Li, Q.; Chen, G. Decomposition rule of hydrate injection inhibitor in pilot plant. *Chem. Prog.* **2022**, *41*, 1–13. [CrossRef]
- 29. Zhang, G.Q. Mechanism analysis of the effect of electrolytes and alcohols on the phase balance of natural gas hydrate. *Guangzhou Chem. Ind.* **2020**, *48*, 17–20.
- 30. Sun, Z.N. *Molecular Simulation of Hydrate Decomposition Mechanism under the Action of Inhibitors;* China University of Petroleum: Qingdao, China, 2015.
- Ding, T.; Wang, R.; Xu, J.; Wang, X.; Yu, Z.; Cheng, Y.; Wang, Z. Experimental study and modeling of methane hydrate dissociation by depressurization and chemical injection. In Proceedings of the 29th International Ocean and Polar Engineering Conference, Honolulu, HI, USA, 16 June 2019.
- 32. Peng, L. Study on the Decomposition Law of Methane Hydrate in the Presence of Inorganic Salts; China University of Petroleum: Qingdao, China, 2017.
- 33. Zhang, Z.X.; Xu, L.; Zhang, T.J. Molecular simulation of the mechanism of hydrate decomposition of inorganic salts. *Inn. Mong. Petrochem. Ind.* **2020**, *46*, 16–22.