energies

Review

A Review of Gas Capture and Liquid Separation Technologies by CO_2 Gas Hydrate

Sergey Misyura [1,*], Pavel Strizhak [2], Anton Meleshkin [1], Vladimir Morozov [1], Olga Gaidukova [2], Nikita Shlegel [2] and Maria Shkola [2]

[1] Kutateladze Institute of Thermophysics, 630090 Novosibirsk, Russia
[2] Heat and Mass Transfer Laboratory, National Research Tomsk Polytechnic University, 634050 Tomsk, Russia
* Correspondence: misura@itp.nsc.ru

Abstract: Gas hydrates, being promising energy sources, also have good prospects for application in gas separation and capture technologies (e.g., CO_2 sequestration), as well as for seawater desalination. However, the widespread use of these technologies is hindered due to their high cost associated with high power consumption and the low growth rates of gas hydrates. Previous studies do not comprehensively disclose the combined effect of several surfactants. In addition, issues related to the kinetics of CO_2 hydrate dissociation in the annealing temperature range remain poorly investigated. The presented review suggests promising ways to improve efficiency of gas capture and liquid separation technologies. Various methods of heat and mass transfer enhancement and the use of surfactants allow the growth rate to be significantly increased and the degree of water transformation into gas hydrate, which gives impetus to further advancement of these technologies. Taking the kinetics of this into account is important for improving the efficiency of gas hydrate storage and transportation technologies, as well as for enhancing models of global climate warming considering the increase in temperatures in the permafrost region.

Keywords: CO_2 hydrate; gas sequestration; desalination; kinetics; greenhouse gases

Citation: Misyura, S.; Strizhak, P.; Meleshkin, A.; Morozov, V.; Gaidukova, O.; Shlegel, N.; Shkola, M. A Review of Gas Capture and Liquid Separation Technologies by CO_2 Gas Hydrate. *Energies* **2023**, *16*, 3318. https://doi.org/10.3390/en16083318

Academic Editor: Attilio Converti

Received: 14 March 2023
Revised: 28 March 2023
Accepted: 6 April 2023
Published: 7 April 2023

1. Introduction

Gas hydrates are ice-like deposits consisting of water and gas. Typically, the prevailing gas is methane. Gas hydrates are non-stoichiometric compounds. Water molecules form cage-like structures in which gas molecules are enclosed as guest molecules [1–3]. Gas hydrates exist in a stable state at very high pressures and relatively low ambient temperatures. Huge deposits of natural gas hydrates are located underneath the oceans and in permafrost regions.

Gas hydrates may consist of different types of gas molecules and be sustainably stored for a long time under different equilibrium conditions. In addition to the predominant gas (methane), natural gas hydrates may also contain hydrogen sulfide (H_2S), carbon dioxide (CO_2), as well as other hydrocarbons, though much less frequently. Hydrates usually form one of three different repeating crystal structures: structures I (sI), II (sII) (a cubic system) and the third structure (H) [2–4]. All three structures are implemented in natural conditions, with the sI being the most common.

Cages of structure I contain smaller gas molecules. The source of such molecules, placed in a crystal structure, is a biogenic gas, widespread in the ocean bed deposits.

The unit cell of sII consists of 24 cages (16 small cages and 8 large cages, which are larger in size than in sI). Natural gas hydrates with sII contain mixtures of gases with molecules that are larger in size than the ethane molecule, but smaller than the pentane molecule. The sH is more complex than sI and sII [1,2,5] and contains a cage type with very large gas molecules (e.g., methyl cyclohexane). The sH hydrates occur naturally in reservoirs in Barkley Canyon, the Gulf of Mexico, the Caspian Sea and Blake Ridge [6,7].

The reservoirs contain hydrocarbons such as neohexane, isopentane, methylcyclopentane and methylcyclohexane.

There are various estimates of natural gas reserves in the form of gas hydrate deposits. Initial estimates of these reserves ranged between 1.8×10^{16} m^3 and 2×10^{16} m^3 [8]. The highest estimates of natural reserves (3×10^{18} m^3) were based on the assumption that the gas hydrates occupy the entire floor of the deep ocean [9–11]. By now, it has been established that the gas hydrates are localized in a narrow depth range (continental shelves) and that the concentration of gas (methane) there is usually low. Approximate estimates show that natural gas reserves range between 1×10^{15}–5×10^{15} m^3 [12,13], which is below the first estimates received. The last estimates of natural gas reserves are confirmed by a model for predicting the distribution of methane gas hydrate in marine sediments [14]. After all, these reserves are a huge promising source of energy for future generations. In addition, due to climate change, the reserves of methane and carbon dioxide can have a substantial impact on climate change on the planet [15,16].

Geo-hazards associated with gas hydrate deposits are usually divided into global and regional by types of threat. Global climate threats are particular to deep-sea gas hydrate deposits, as well as reserves of natural gas hydrates in permafrost zones. Existing models of climate warming demonstrate a more moderate increase in temperature. The faster warming is assumed to be associated with the additional release of greenhouse gases from gas hydrate deposits, which may increase in the future and requires more intensive scientific research [15]. So, in recent decades, there has been a noticeable retreat of the permafrost zone. Predictive estimates of global warming (the IPCC 2007) [15] show that by about the year 2100, the mean surface temperature may increase from 1.1 °C to 6.4 °C. The most likely warming prognosticates an increase in temperature by 4 °C. These estimates refer to the impact of both the oceans and the permafrost regions. The strongest warming is ascribed to the permafrost regions in the Northern hemisphere. So, by 2100, warming in these areas may reach 12 °C [16].

To date, there are no reliable data on methane reserves in and under permafrost hydrates in the Arctic and Antarctic. Therefore, it is difficult to estimate the amount of gas released due to warming. At the same time, there are estimates that suggest a significant increase in the amount of methane in the permafrost region on the East Siberian Arctic shelf [17–19]. It is assumed that the underwater permafrost is extremely sensitive to regional warming and covers gas hydrate reserves around the world.

Existing climate warming models are also indicative of the future noticeable increase in water temperature (IPCC 2007). Seawater at a depth of 200 to 1500 m washes sediments that contain gas hydrates. However, estimates of the gas release into the atmosphere and, accordingly, the temperature increase due to the dissociation of gas hydrates vary greatly because of the high uncertainty of the gas content in gas hydrates in these areas [20–23]. The models predict that the release of methane can add an extra temperature increase of 0.5 °C to global warming without regard to additional water heating. Thus, further studies are necessary to estimate the amount of methane and other greenhouse gases in and under gas hydrate deposits. Moreover, it is expedient to further develop models of stability limits of these deposits, depending on the natural conditions and the composition of the deposits.

2. Combating the Warming by Reducing Anthropogenic Emissions and CO_2 Separation

Aside from the causal link between natural gas hydrates and climate warming, it is also extremely important to pay attention to warming issues associated with human activities. High industrial carbon dioxide emissions can also have a negative impact on the climate. Earlier, emphasis was placed on the growing influence of methane emissions, formed during the dissociation of natural gas hydrates, on climate warming. However, carbon dioxide, which belongs to anthropogenic greenhouse gases, also plays an important role in climate change. Over the past 30–40 years, there has been an increase in annual CO_2 emissions by more than 70–80%. To date, the share of carbon dioxide in the total amount of anthropogenic greenhouse gases (according to forecasts of the Intergovernmental Panel on Climate Change (IPCC)) is approximately 75–80% [15]. Therefore, it is carbon dioxide emissions that increased attention is paid to. Estimates testify that due to the increase in CO_2 emissions, the average global temperature on the planet may increase by 1.9 °C as early as in 2100 [24].

It is generally recognized that in order to reduce the negative impact of anthropogenic emissions, it is necessary to develop alternative environmentally friendlier energy technologies [25,26]: for example, nuclear power, biotechnology, biomass processing, as well as actively developing solar and wind energy. However, today environmentally safe technologies can meet only a small part of modern energy needs.

In the coming decades, common fossil fuels will remain the major ones due to their low production costs, as well as ease of storage and transportation. Therefore, in the near future it will be impossible to significantly reduce CO_2 emissions by reducing and reengineering production. A more realistic strategy is aimed at creating highly efficient technologies for the separation and capture of carbon dioxide from industrial emissions. To reduce the cost of these technologies, it is necessary to intensify scientific and technological research in the fields of chemical and physical absorption, membrane technologies and cryogenic separation, chemical and electrochemical technology, biotechnology, as well as separation technologies using gas hydrates [25,26]. In recent years, great attention has been paid to the development of effective technologies for capturing carbon dioxide from industrial flue gases and emissions of the automotive industry. More attention has been given to the issues of carbon dioxide storage in natural reservoirs, technologies of gas separation, water desalination, gas storage and transportation, as well as refrigeration technologies based on gas hydrates.

Consideration has been also given to the monitoring of methane reserves included in natural gas hydrates, as well as gas hydrates with carbon dioxide. Due to the high solubility of carbon dioxide in seawater, as well as the high compressibility of liquid CO_2 relative to seawater, liquid carbon dioxide acquires neutral buoyancy at a sea depth of 2500–3000 m [27]. One of the most well-known methods of probing deep-sea reserves of natural gas and CO_2 in the form of gas hydrates is marine sounding using the geophysical electromagnetic method (CSEM technology), which employs an electric dipole source placed above the seabed. This source transmits a time-varying electromagnetic field. The CSEM technology facilitates remote mapping of subsurface resistivity distribution without the need to drill additional wells. Carbon dioxide has less conductivity than an environment without CO_2. Therefore, with sufficient sensitivity of the method, it is possible to distinguish peaks of conductivity changes at a certain depth. The influence of the electromagnetic field on the kinetics of gas hydrate growth, as well as on the monitoring of a formation containing carbon dioxide, is considered in [26,27]. Geophysical electromagnetic methods are widely used to monitor sequestration of carbon dioxide in an environment with seawater [27].

The technology of separation of gas hydrates is relatively new and rapidly developing. The method of successful separation of propane and propylene using gas hydrates served as the basis for the rapid progress of this technology, which successfully switched to the technology of separation of mixtures [28,29] and carbon dioxide capture. Integrated Gasification Combined Cycle of syngas with the use of gas hydrates is already being applied today and garners great interest. Economic estimates show the high efficiency of CO_2 separation by the gas hydrate method in comparison with other generally accepted methods [30]. The rapid formation of carbon dioxide hydrate is due to the fact that the pressure at CO_2 hydrate formation is much lower than that of nitrogen. Thus, at the ice melting temperature, the equilibrium pressure for the formation of carbon dioxide hydrate is approximately 1.2 MPa, and for nitrogen hydrate it is approximately 16 MPa.

CO_2 hydrates are separated and dissociated to obtain a gas stream with a high content of carbon dioxide in the pipeline, which is not connected to the external atmosphere. One of the important problems of this technology is the need to create a high equilibrium pressure for the formation of hydrates. The physical and chemical features of this technology are considered in [31,32]. An important method for increasing efficiency is the use of promoters, which allow the reduction of the pressure with the growth of the gas hydrate. The advancement of these technologies requires joint research of scientific and scientific–technical centers dealing with various fields of physics, chemistry and geology.

Another important problem is related to gas extraction from gas hydrate deposits. It can lead to the loss of strength and subsidence of the seabed [33,34]. The elimination of such negative consequences and geological hazards requires a non-destructive method of methane recovery using carbon dioxide or the flue gas injection into natural reservoirs of gas hydrates [35–42]. This method provides simultaneous performance of both the methane recovery function and the CO_2 separation capture function. The injection of flue gases from industrial waste can be realized without additional separation of carbon dioxide [41–43]. The largest number of studies is associated with CH_4–CO_2 replacement in sI hydrates [36,37,43–46]. sH hydrates are also sometimes found at significantly lower depths of seawater. The smaller drilling depth makes sH hydrates more convenient for extracting methane and injecting carbon dioxide [47,48].

3. The Use of Gas Hydrates Containing Carbon Dioxide

3.1. The Gas Separation Using Gas Hydrates Containing CO_2

The largest number of studies on CH_4–CO_2 replacement concerns gas hydrates with sI [49–57]. The introduction of the carbon capture and sequestration technologies requires huge expenditures, which slows down their development, and also explains the insufficient pace of combating flue gas emissions. The use of gas hydrates for the problems of CO_2 capture and sequestration significantly increases the technology's efficiency [58]. However, in order to reduce the cost of storage, transportation and disposal, there is a need for additional studies, which will be considered later.

The submarine geological storage of carbon dioxide based on gas hydrates is one of the most effective methods. The heat flux from the ambient medium and the hydrate volume fraction have an essential effect on the dissociation process and the stability of the gas hydrate [59]. The possibilities and prospects for the development of the technologies of the hydrocarbon industry for carbon capture, utilization and sequestration are considered in [60]. The CO_2 injection into natural gas hydrate reservoirs is discussed in [49–62]. These methods avoid the need in the initial creation of a gas hydrate with carbon dioxide and the pressure drop for hydrate formation using promoters, since gas hydrate deposits have a large depth and high pressure in the rock. Huge natural reserves of gas hydrates also open up a great prospect for the utilization of greenhouse gases. However, there remains the problem of delivering the flue gas from industrial enterprises to remote places of natural deposits.

The processes of the dissociation of gas hydrates at great depths are realized in porous media. Therefore, it is important to investigate the effect of various porous media on the kinetics of the growth and dissociation of gas hydrates. The technologies of the CH_4/CO_2 replacement for CO_2 sequestration in porous media are considered in [63]. This paper discusses the key mechanisms of hydrate formation in various porous media and provides an analysis of the gas hydrate formation in various porous materials: activated carbon; solid and hollow silica with nanoparticles; glass beads. Furthermore, the matter in question here is problems and limitations in the replacement process, considering: effects on the use of secondary gas; effects of kinetic and thermodynamics promoters; effects of carbon dioxide state and pressure; effects of porous media, thermal stimulation and saturation. Amidst the restrictions on the use of this technology are the low output of methane and a slow rate of replacement due to an impenetrable barrier of CO_2 hydrate film formed on the gas hydrate surface. These problems significantly impair the economic efficiency and implementation of this technology [63].

The analysis of the technologies of methane production and CO_2 storage using the natural gas hydrate-bearing sediment is given in [64]. The paper shows that the depressurization-assisted replacement could surmount the weakening of the geo-mechanical strength of the sediment for depressurization only, and the slow production rate for replacement only. It would be useful for low-carbon energy production from the natural gas hydrate-bearing sediments.

For carbon dioxide utilization, taking into account the location of gas hydrate deposits, the depth of gas hydrates corresponds to 1000–2500 m. At such a great depth, quite high pressures and temperatures are realized: hundreds of degrees Celsius and hundreds of bars [65]. Various methods are used to utilize carbon dioxide and simulate the dissociation of natural gas hydrate using wells of great depths. Effective methods of extraction, as well as analysis of data from natural reservoirs are given in [66].

The influence of physical and chemical features of gas hydrates on their technical application and prospects for the technology development, including hydrates with carbon dioxide, is described in [67]. The presence of carbon dioxide hydrate reduces the permeability of the formation, which inhibits the dissociation of methane hydrate and diminishes the efficiency of methane extraction from the formation [68]. At that, the presence of CO_2 hydrate increases the strength of the formations (layers) and decreases the probability of sand occurrence.

Various key factors have an important influence on the gas hydrates exploitation with CO_2 replacement: the phase state of the carbon dioxide used for injection; thermodynamic conditions during the synthesis of CO_2-based gas hydrate; the type of auxiliary gases used (for example: nitrogen, hydrogen, air); the structural parameters of the gas hydrate; and the hydrate saturation in the rock [69]. This paper also examines the limitations and prospects for further research of technologies using CO_2 replacement.

Natural reservoirs can be efficient to store carbon dioxide, combining the extraction of methane and the disposal of harmful and greenhouse gases. The combination of natural hydrates exploitation and CO_2 storage is considered in [70]. After a long-term reformation, the methane recovery ratio increased from 24% to 85%. In addition, the CO_2 storage ratio was raised to 79–80%. The study of the micro-scale characterization of the sI hydrates containing a mixture of CH_4 and CO_2 was performed in [71]. A comparison of the technical and economic indicators of CO_2 separation technologies (at a high carbon dioxide content in natural gas) based on membranes and the controlled freeze zone separation is given in [72].

Much attention in terms of increasing gas production is paid to the following methods: thermal stimulation with CO_2 and N_2 injection [73], the cycling depressurization method [74], and using electrical heating [75].

The metal–organic framework and gas hydrate synergy is an effective technology for CH_4 storage and CO_2 separation [76]. This review article presents the structural characteristics of the metal–organic framework and gas hydrates, as well as an analysis of restrictions on the storage and separation of carbon dioxide. Metal–organic frameworks (MOF) used for capturing, separating and storing CO_2 usually have a developed micro–nano pore system, which allows for a large pore volume and a high specific surface area of a porous material [76,77]. The wider application of the metal–organic frameworks necessitates additional research on the kinetics of the physical sorption of gas molecules on the metal surface, MOF water resistance and the effect of nano-retention and properties of water in nanopores.

The addition of a small amount of carbon dioxide (about 15%) to the air stream (nitrogen) leads to an increase in methane production by almost 25%. It has been found that the optimal ratio (mole ratio of carbon dioxide to methane) corresponds to 1.3–1.45 [78]. Small additions of nitrogen and hydrogen to the gas mixture can not only increase methane production, but also prevent CO_2 liquefaction [79]. The injection of CO_2/H_2 gas mixture allows a high efficiency of natural gas hydrate exploitation and carbon sequestration to be achieved [80]. In CO_2/H_2 gas phase systems, several gas hydrates with different phase equilibrium temperatures can be formed [81]. The growth of gas production from gas hydrate deposits due to CH_4–CO_2/H_2 is described in [82]. The efficiency of gas extraction and the use of the promoter depend on the type of gas mixtures: flue gas ($CO_2/N_2/O_2$); sulphur hexafluoride (SF_6); and gas mixture (SF_6/N_2) [83–86].

Modeling of the kinetics of growth and dissociation of hydrates with carbon dioxide is considered in [87–90]. To simulate the conditions of dissociation and synthesis at such great depths, the accuracy of the models should be increased. Most of the reliable calculation methods deal with the moderate depths of natural gas hydrates. The model of brine systems ($CO_2/CH_4/H_2S/N_2$) for simulating a non-isothermal multicomponent system in the presence of high temperatures and pressures is discussed in [91]. Modeling of the process of growth and dissociation of carbon dioxide hydrate, taking into account heat and mass transfer, is described in [92–97]. The numerical study of the gas hydrate formation during the gas injection into a porous medium is considered in [98].

The application of molecular dynamics (MD) methods related to carbon dioxide-based hydrates is explained in [87–89]. Modeling of CO_2 replacement of CH_4 hydrate using MD methods is demonstrated in [87]. The use of MD for the growth of carbon dioxide hydrate in the presence of an electric field is considered in [88,89]. Modeling of the formation and dissociation of carbon dioxide hydrate in porous media is presented in the review article [89]. The analysis of kinetic mechanisms on the natural gas hydrate replacement by CO_2 is considered in [99].

The warm brine injection during CH_4/CO_2 replacement process enhances the intensity of heat and mass transfer and the reaction rate [100]. Great attention is paid to the issues of hydrate formation in seawater. The key points on the desalination of seawater using carbon dioxide hydrates are discussed in Section 3.3.

3.2. The Use of Promoters to Increase the Efficiency of the Growth of Gas Hydrates

To develop the technology for the efficient separation of carbon dioxide from the flue gas, it is necessary to use various mechanisms: lowering the temperature and pressure; reducing the induction time and increasing the nucleation rate; and increasing the rate of hydrate growth and the gas content in the gas hydrate. Within the frameworks of these tasks, the effect of various surfactants on the equilibrium parameters, gas solubility, surface properties of gas hydrate (for example, surface tension), as well as on the morphology of growing hydrate particles are investigated.

High equilibrium pressure at the formation of hydrates with carbon dioxide noticeably increases the cost of CO_2 capture technology based on gas hydrate technology. To reduce the cost of the technology, both the equilibrium temperature and the equilibrium pressure were reduced using various promoters. Tetrahydrofuran (TF) was chosen as one of the first promoters [101]. In this paper, the regularities of the CO_2 recovery from the flue gas by the formation of a gas hydrate were investigated. Using the three-stage separation process, a high degree of purification of the gas mixture from carbon dioxide was achieved (up to 99% in the temperature range of 273–283 K) at a concentration of 17% carbon dioxide in the gas mixture. However, the induction time of crystallization remained quite large. Reducing the induction time, in addition to increasing the gas hydrate rate, is an important parameter for enhancing the efficiency of the separation process.

An environmentally friendly promoter for the growth rate of gas hydrates is Tetra-n-butyl ammonium bromide (TBAB), which forms a semi-hydrate with water molecules and gas molecules. The equilibrium conditions, as well as the dissociation enthalpy of the semi-hydrates, were investigated in [102–104]. The use of TBAB allows the conditions for the formation of the semi-hydrate to be significantly simplified [105].

Forming the Tetra-n-butyl ammonium bromide semi-clathrate hydrate substantially reduces the induction time of the gas hydrate formation. Carbon dioxide is purified from 17.0 mol% to 99.4% with two-stage hydrate separation (the CO_2 split fractions for stage 1 and stage 2 are 0.54 and 0.39, and the separation factors are 9.6 (stage 1) and 62.2 (stage 2)) [106]. The medium-pressure clathrate hydrate/membrane hybrid process is used to purify flue gas that includes carbon dioxide with a concentration of 16.9% [31]. The use of Tetrahydrofuran increases the gas hydrate growth rate compared to the pure water system [84]. The use of sodium dodecyl sulfate and anionic fluorosurfactant to capture and sequester carbon dioxide from the gas mixture (N_2 and CO_2) was considered in [107]. The regularities of the gas separation and storage of the CO_2-TBAB semi-clathrate hydrate were performed in [108]. With the growth of TBAB concentration in aqueous solution, the CO_2 separation grows, reaching maximum, and further (while exceeding the mass concentration of 35%) changes slightly. TBAB semi-clathrate hydrate increases the hydrate stability at its formation [109]. The CO_2 separation from the gas mixture (N_2 and CO_2) using the semi-clathrate hydrates with TBAB (0.29 mol%) and with dodecyl trimethyl ammonium chloride was investigated in [110]. The study of the hydrate formation, as well as the gas storage capacity of the gas hydrate, was performed in [111]. The use of a hydrate promoter to increase CO_2 separation from the CO_2 and N_2 gas mixture was also studied in [112].

Natural deposits of gas hydrates may contain various surfactants that affect the rates of synthesis and dissociation [1,2,113]. In pure water, the growth rate of gas hydrate is extremely low. The formation of a hydrate crust on the surface of the particles inhibits the front motion into the particle due to slow diffusion. The gas solubility controls the reaction rate and the nucleation mechanisms of CO_2 gas hydrate [114]. The presence of surfactant significantly affects the gas solubility and the gas hydrate formation [115]. One of the first hypotheses on the influence of surfactant explained the effect of accelerating hydrate formation with a decrease in the surface energy of hydrates and with an increase in gas solubility. Thus, the adsorption of surfactant molecules on the free surface of a solid particle leads to an increase in the hydrate formation rate [116]. The relation of hydrates' growth rate to the solubilization effects was also indicated in [101]. Another point of view on the faster kinetics of hydrate growth was associated with the morphology of hydrates. It has been shown that in the presence of surfactants, the surface of the gas hydrate ceases to be a solid and durable crust. Surfactants make the surface of the gas hydrate loose and porous [117,118]. The capillary force allows the solution to move inside the porous particle. The formation of dendrites on the solution surface and the presence of capillary force affect the rate of hydrate layer growth [119,120]. The change in kinetics was associated with the mechanisms of concentration diffusion, micelle formation and deposition of surfactant crystals. Another key role in the growth of the hydrate formation rate was associated with micelles [121–123].

Characterization of clathrate hydrates formed with CO_2 and tetrahydrofuran (THF) is considered in [124,125]. The phase behavior of CO_2 gas hydrate in the presence of tetrahydropyran (THP) is investigated in [126–128]. The reduction of hydrate formation pressure is influenced by cyclopentane (CP) [127,129–131], cyclobutanone and cyclohexane (CH) [128], 1,3 Dioxolane [132], 1,3,5 Trioxane [133]. In practice, tetrabutyl ammonium and phosphonium salt are often used [102–106,134,135]. The growth rate of CO_2 gas hydrate increases with the use of sodium dodecyl sulfate (SDS) [115,136], Tween [137] and Dodecyltrimethylammonium chloride (DTACl) [137]. The advantages and disadvantages of different gas hydrate promoters and porous materials, as well as the analysis of the properties of CO_2 hydrates at the molecular level are given in [138].

The effect of reaction promoters in the form of graphene nanoparticles is given in [139]. The use of graphene and SDS solutions can significantly accelerate the CH_4 hydrate formation and increase the CO_2 sequestration ratio. The analysis of the use of highly effective kinetic and thermodynamic promoters to increase the growth rate of gas hydrates, as well as to increase the stability of natural gas hydrates, is presented in [140]. The promoter in the form of hydrophobic fluorinated graphene provides a high growth rate of carbon dioxide hydrate, as well as the high storage capacity [141]. The classification of promoters for CO_2 hydrate formation is presented in Table 1.

Table 1. Classification of promoters for CO_2 hydrate formation.

Classes Promoters	Action Principle	Some Types of Promoters
thermodynamic	Reduces the pressure or increases the temperature of hydrate formation.	Tetrahydrofuran (THF) [101,124,125] Tetrahydropyran (THP) [126–128] Cyclopentane (CP) [127,129–131] Cyclobutanone [128] Cyclohexane (CH) [128] 1,3 Dioxolane [132] 1,3,5 Trioxane [133] Tetra-n-butylphosphonium acetate (TBP-Ace) [127] Tetra-n-butyl ammonium bromide (TBAB) [102–106] Tetra-n-butyl ammonium nitrate (TBANO3) [134] Tetra-n-butylphosphonium bromide (TBPB) [135] Tetra-n-butyl phosphonium chloride (TBPC) [135]
kinetic	Enhances the kinetics of hydrate formation without affecting the thermodynamics	Sodium dodecyl sulfate (SDS) [115,136] Tween [137] Dodecyltrimethylammonium chloride (DTACl) [137] L-methionine [127,138] L-norvaline [127,138] L-norleucine [127,138] L-glycine [127,138] L-tryptophan [127,138] Metal particles and metal oxides [138] Nanotubes [138] Graphene [138,139,141]

Despite numerous studies of surfactants, there is currently no clear understanding of which of these factors are more important for the kinetics of formation and growth of gas hydrates. Most likely, the majority of factors are important at different stages: dissolution and diffusion of gas, formation of nuclei, growth of hydrate particles. For the rapid and effective separation of carbon dioxide from the flue gas due to gas hydrates, it is necessary not only to lower the temperature and equilibrium pressure, but also to reduce the induction time and increase the rate of gas hydrate and the carbon dioxide content in the gas hydrate. For these purposes, it is important to use different types of promoters simultaneously. It is also important to solve the problems of increasing the efficiency of storage and transportation of the obtained hydrates with the presence of carbon dioxide, which were synthesized using various promoters.

3.3. Desalination of Water and Release of Harmful Impurities Using a Gas Hydrate Containing Carbon Dioxide

In the previous paragraph, the issues of climate change due to greenhouse gases and technologies for combating atmospheric pollution through the use of CO_2 hydrate were discussed. The problems related to water desalination, as well as the purification of various media from harmful impurities, are also of great interest. These areas of research are also associated with global environmental problems. Wastewater discharges from domestic and industrial enterprises have increased significantly in recent decades, leading to an increase in soil contamination with metal ions [142,143]. Wastewater may contain hazardous materials, non-toxic organisms, bacteria, viruses, sewage, detergents and garbage.

As a result of the activities of the industrial chemical industries, a huge number of heavy metals enters wastewater every year: Cr, As, Pb, Zn, Ni, Cu and Cd. Since metals are easily dissolved in an aqueous medium, their concentration often reaches high values exceeding human safety limits [144]. The features of the application of technologies for the purification of heavy metals and their harm to the human body are considered in [145–147].

In addition to heavy metals, a huge number of toxic substances dangerous to human health appears in the environment every year: oil, aromatics, pesticides and dye [148–152].

The most commonly used technologies for the purification of aqueous solutions from heavy metals are associated with the electrochemical method, the use of membranes, the adsorption and chemical deposition of impurities [153]. These methods are technologically advanced, but still have significant drawbacks: not a very high degree of liquid purification from metal, significant limitations on the selectivity of various types of metal, the formation of a large amount of waste after cleaning, the formation of sludge, as well as significant energy consumption for cleaning. Due to the deterioration of the environmental situation, it is necessary to develop alternative technologies. One of these methods is wastewater treatment using gas hydrates [1,5,142,146]. This technology significantly increases the efficiency of the release of impurities in the form of dissolved minerals and heavy metals, but is still highly energy consuming. The low growth rates of gas hydrate should be also noted. Therefore, for the development of technologies based on gas hydrates, further research is needed to increase the growth rate and reduce energy consumption.

The effective technology development through the use of gas hydrates is hindered due to the rather slow kinetics of hydrate growth, as well as due to problems associated with the removal of salt from the hydrate (hydrate solution with salt) and with clogging the crystal surface with salt. A conveyor belt can be used to separate the crystals. Dissociation is realized in different compartments using a non-stirred reactor. Another method is associated with the uprise of hydrates, formed at great depth, due to buoyancy and with the hydrate washing with water [154]. The use of liquid propane (as a hydrate-forming agent) at the bottom of the reactor zone turns out to be a fairly effective method of desalination. The formed hydrate ascends to the water surface due to buoyancy. Separation plates ensure effective separation of hydrate crystals from the salt solution [155]. To apply the heat of hydration for the hydrate dissociation (and as a solvent for the formation of hydrate), a heat exchange liquid that does not mix with water is used [156]. The hydrate suspension and its extraction to the surface, as well as the use of pipelines and columns are considered in [157,158]. The deposition of hydrate crystals during their formation, the usage of a conveyor belt and the transportation of washed hydrates to the dissociation region are considered in [159]. The formation of a thick layer of hydrate blocks the flow of salt water. The resulting hydrate is separated when the pressure decreases [160,161]. The applied blend of hydrochlorofluorocarbons, hydrofluorocarbons and chlorofluorocarbon molecules decreases the dendritic growth of hydrate. Ice formation on top of hydration and salt leaching (on the hydrate surface) during ice melting using a vertical tubular reactor is considered in [162]. The employment of hydrate-forming gas (microbubbles), which is pumped into a reactor with salt water, is discussed in [163]. The formation of CO_2 hydrate in 2 wt. % brine solution allows achieving the high removal efficiency of 60.08% [164]. The application of graphene helps to solve the problem of filtration and desalination of water [165].

A comprehensive review on the application of clathrate hydrates as a promising carrier for water desalination/treatment is presented in [166]. Problems and prospects of development of the hydrate-based desalination technology are discussed in [167]. A review of the latest achievements, technological potential and disadvantages of heavy metal removal methods, as well as industrial wastewater treatment systems was made in [168]. Fundamental properties of gas hydrate formation, including CO_2 hydrate, thermodynamic and kinetic aspects and energy consumption are described in the review article [169].

The use of hydration, as well as carbon dioxide during hydrate formation, serves to purify the aqueous solution from salt, as well as to separate CO_2 and solve the issues of carbon dioxide storage (greenhouse gas utilization) [170–173]. The installation of the continuous production and granulation of CO_2 hydrate is demonstrated in [174]. This unit is used to investigate the removal efficiency of salt ions in water–salt solution. The employment of carbon dioxide, as well as the water-immiscible formers to form double hydrates, provided for a high salt removal rate (over 90%) [175]. Experimental results of the hydrate formation in the presence of carbon dioxide, as well as mixed formers containing carbon dioxide, are given in [176–180].

Molecular dynamic (MD) simulation of the interaction of methane and water gas molecules, the CO_2 hydrate nucleation and the hydrate growth are considered in [181–187]. The mechanism of methane hydrate formation by replacing carbon dioxide molecules was investigated using MD simulation in [186]. It has been found that a large amount of hydrate residues (in methane hydrate) facilitates the nucleation of the CO_2 hydrate and accelerates the hydrate growth [187].

Water volume affects the CO_2 hydrate-based desalination. With an increase in water volume from 300 mL to 500 mL, the removal efficiency increases from 31% to 60% [188]. The kinetics of the growth of CO_2 hydrate in a porous medium is studied in [189]. CO_2 hydrate has a faster growth kinetics in quartz sand compared to an aqueous salt solution. In this porous medium, the hydrate conversion reaches 87% compared to 55% in a water-salt system.

To improve desalination efficiency, a hybrid desalination process, using carbon dioxide gas hydrate and capacitive deionization with synthesized electrodes based on the activated carbon and their chemical properties modified using nitric acid, is proposed in [190]. This method allows removing about 82% of Na^+, 100% K^+, Ca^{2+} and Mg^{2+} ions from salt water.

Tetrahydrofuran and cyclopentane are used as effective thermodynamic promoters of reactions for the liquid hydrate formers of sII [191–202]. As mentioned above, the slow kinetics of hydrate growth, as well as the low temperature and high pressure of hydrate formation, hinders the effective development of desalination technology. The thermodynamic promoter, cyclopentane (6 mol %), increases the hydrate formation temperature from 277 to 291 K at a pressure of 2.0 MPa [191].

Tetrahydrofuran is water-miscible, while CP is a water-immiscible strong thermodynamic promoter, easily removed from water. In addition, cyclopentane forms gas hydrates at atmospheric pressure [192]. Morphology and kinetic studies of cyclopentane are performed in [193–200]. Thermodynamics and structural parameters of cyclopentane/CO_2 hydrates, as well as the kinetics of their dissociation kinetics are considered in [201]. Studies using the X-ray diffraction have shown that the large cages of the cyclopentane/CO_2 sII hydrates s are completely filled with gas molecules, while the small cages are filled with CO_2 by only 62%. It has also been found that the presence of salt molecules in water slows down the growth of gas hydrate. Experiments and simulations of the phase equilibrium and dissociation of CO_2 with cyclopentane hydrate in an aqueous salt solution for CO_2 capture are given in [202].

3.4. Dissociation of CO_2 Hydrate at Temperatures below the Melting Point of Ice

As indicated in the Introduction, climate warming leads to a significant decrease in the permafrost area, which results in the release of a large amount of greenhouse gases. In addition, the storage of natural gas in the fields at subzero temperatures in the northern regions also creates additional scientific and technological problems. For example, the dissociation of natural gas hydrate or CH_4–CO_2 replacement (during the extraction of natural gas) can be realized at negative temperatures (at temperatures below the melting point of ice).

The kinetics of the gas hydrate dissociation at negative temperatures differs from that at positive temperatures and very high pressures, when deposits of natural raw materials are located at great depths.

The stability zone of gas hydrates in the permafrost region is related to the depth range of 200–2000 m. However, the occurrence of self-preservation at temperatures below the ice melting point leads to the long-term existence of gas hydrates at depths less than those indicated [203,204]. Thus, core samples of frozen rocks of the northern hemisphere demonstrate the presence of gas hydrates at a depth of 70–120 m. There is an intensive release of natural gas and CO_2 when drilling wells in cryolithozones, containing relict hydrate-bearing layers. Rapid freezing of the rock is assumed to lead to a sharp jump in pressure at the freezing front due to water and gas accumulation. Thus, even short-term freezing of the rock leads to the appearance of gas hydrates and their long-term storage.

Another important area related to gas hydrates (including hydrates with carbon dioxide) is related to storage and transportation issues. The carbon dioxide hydrates obtained during the purification of industrial gas waste, as well as those obtained as a result of desalination technology, must be stored for a long time. Long-term storage of gas hydrate raw materials at negative temperatures is effective due to the phenomenon of self-preservation.

Self-preservation is understood as a phenomenon when abnormally low dissociation rates of gas hydrate are realized in the temperature range of 230–267 K [205–211]. So, if a gas hydrate covered with a thin shell of ice is stored in a given temperature range, then the half-life of the gas hydrate can reach several weeks or months. The high strength of the ice shell is achieved due to the small size of ice grains (about 10–50 µm), which are formed during the dissociation of gas hydrate [205,207,208].

The phenomenon of self-preservation also manifests itself at high heat fluxes, when the external temperature can reach high values, and the temperature of the gas hydrate is below the freezing point [212–215]. To increase the storage time of gas hydrates, powder pressing (tableting) is used, which significantly reduces the dissociation rate [216]. The most optimal diameter of gas hydrate particles for long-term storage is ≈1 mm [217–219]. The smaller particle size leads to a high dissociation rate. It is inefficient to use larger diameters of individual particles because of the very low growth rate (during the synthesis of gas hydrate) and high energy costs. The combined effect of porosity, permeability and particle size is described in [220]. Ways to increase the storage efficiency of natural and artificial methane hydrates at subzero temperatures are considered in [221].

A study on the decomposition effect on the replacement of the CO_2–CH_4 hydrate in hydrate-bearing sediments below the freezing point is presented in [222]. The kinetics of CO_2 hydrate dissociation (activation energy and pre-exponential multiplier) at negative temperatures differs from dissociation at positive temperatures [223–225]. When using a CO_2 hydrate to extinguish a flame, it is also necessary to take into account the kinetics of the gas hydrate dissociation, which determines the rate of carbon dioxide release [226].

Thus, in order to refine the models for forecasting climate and global warming, it is necessary to elaborate the models describing the dissociation of natural gas hydrate deposits in permafrost zones. So, it is crucial to know the exact kinetics of the gas hydrate dissociation, depending on the porosity of the formation, the size of gas hydrate particles, the thickness of the formation, self-preservation, as well as the influence of seasonal temperature fluctuations.

To increase the efficiency of storage and transportation of carbon dioxide hydrate (formed in desalination technologies, separation of heavy metals, utilization of carbon dioxide from flue gases) at negative temperatures, there is a need for further studies on the combined effect of: powder temperature, particle size and pressed granules (tablets), porosity parameters and morphology of structures on the surface of the ice shell.

4. Conclusions

This analysis of existing works has shown that carbon dioxide hydrate has a huge potential for a wide range of applications. The prospects for the development of technologies based on CO_2 hydrate for the separation and capture of gases, as well as for the desalination of seawater are associated with their efficiency enhancement. It is worth noting some important areas of research in this field:

(i) Gas extraction from gas hydrate deposits may lead to the strength loss and subsidence of the seabed. To avoid severe negative consequences and natural hazards, a non-destructive method of extracting methane with carbon dioxide supply for the formation of CO_2 hydrate is used.

(ii) The use of gas hydrates for the CO_2 capture and sequestration significantly increases the technology's efficiency by enhancing transportation and long-term storage of gas hydrates.

(iii) High equilibrium pressure at the formation of hydrates with carbon dioxide leads to a noticeable increase in the cost of CO_2 capture technology. To reduce the cost, the equilibrium temperature is increased and the equilibrium pressure is reduced using various promoters. The applied promoters can substantially slow down the induction time of gas hydrate formation. In this article, various types of promoters were considered.

(iv) The development of technologies for the purification and desalination of reservoir and seawater based on gas hydrates requires further research aiming at significant increase in the growth rate of CO_2 hydrate and concomitant reduction of energy costs.

(v) To increase the duration of CO_2 hydrate storage, it is advisable to apply the phenomenon of self-preservation (abnormally low dissociation rates), which is realized at a temperature of 230–267 K. The half-life of the gas hydrate in this temperature range can reach several weeks or months. The diameter of the synthesized gas hydrate particles which is the most optimal for its long-term storage is 1–2 mm.

(vi) Analysis of the results of experiments, mathematical modeling, bench-scale and industrial tests indicates that enhancement of the efficiency of the CO_2 hydrate use requires additional studies on the effect on the kinetics of hydrate formation and dissociation at negative temperatures: porosity, particle size, self-preservation, thermobaric conditions, as well as the joint influence of several promoters.

Author Contributions: Writing—original draft, S.M.; writing—review and editing, S.M., P.S., A.M., V.M., O.G., N.S. and M.S.; funding acquisition, A.M. All authors have read and agreed to the published version of the manuscript.

Funding: The research was supported by the Russian Science Foundation (project number 22-79-10330), https://rscf.ru/project/22-79-10330/ (accessed on 28 March 2023).

Data Availability Statement: Not applicable.

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

References

1. Sloan, E.D., Jr.; Koh, C.A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL, USA, 2007.
2. Istomin, V.A.; Yakushev, V.S. *Gas Hydrates in Nature*; Nedra: Moscow, Russia, 1992.
3. Sum, A.K.; Koh, C.A.; Sloan, E.D. Clathrate Hydrates: From Laboratory Science to Engineering Practice. *Ind. Eng. Chem. Res.* **2009**, *48*, 7457–7465. [CrossRef]
4. Das, S.; Tadepalli, K.M.; Roy, S.; Kumar, R. A review of clathrate hydrate nucleation, growth and decomposition studied using molecular dynamics simulation. *J. Mol. Liq.* **2022**, *348*, 118025. [CrossRef]
5. Sloan, E.D., Jr. Fundamental principles and applications of natural gas hydrates. *Nature* **2003**, *426*, 353–359. [CrossRef]
6. Lorenson, T.D.; Collett, T.S. Gas content and composition of gas hydrate from sediments of the southeastern North American continental margin. *Proc. Ocean Drill. Progr. Sci. Results* **2000**, *164*, 37–46. [CrossRef]
7. Lu, H.; Seo, Y.T.; Lee, J.W.; Moudrakovski, I.; Ripmeester, J.A.; Chapman, N.R.; Coffin, R.B.; Gardner, G.; Pohlman, J. Complex gas hydrate from the Cascadia margin. *Nature* **2007**, *445*, 303–306. [CrossRef]
8. MacDonald, G.J. Role of methane clathrates in past and future climates. *Clim. Chang.* **1990**, *16*, 247–281. [CrossRef]
9. You, K.; Flemings, P.B.; Malinverno, A.; Collett, T.S.; Darnell, K. Mechanisms of Methane Hydrate Formation in Geological Systems. *Rev. Geophys.* **2019**, *57*, 1146–1196. [CrossRef]
10. Chen, X.; Lu, H.; Zhang, J.; Ye, J.; Xie, W. Economic Critical Resources for the Industrial Exploitation of Natural Gas Hydrate. *Acta Geol. Sin.* **2022**, *96*, 663–673. [CrossRef]
11. Pang, X.Q.; Chen, Z.H.; Jia, C.Z.; Wang, E.Z.; Shi, H.S.; Wu, Z.Y.; Hu, T.; Liu, K.Y.; Zhao, Z.F.; Pang, B.; et al. Evaluation and re-understanding of the global natural gas hydrate resources. *Pet. Sci.* **2021**, *18*, 323–338. [CrossRef]
12. Milkov, A.V. Global estimates of hydrate-bound gas in marine sediments: How much is really out there? *Earth Sci. Rev.* **2004**, *66*, 183–197. [CrossRef]
13. Milkov, A.V.; Sassen, R. Economic geology of offshore gas hydrate accumulations and provinces. *Mar. Petrol. Geol.* **2002**, *19*, 1–11. [CrossRef]
14. Buffett, B.; Archer, D. Global inventory of methane clathrate: Sensitivity to changes in the deep ocean. *Earth Planet. Sci. Lett.* **2004**, *227*, 185–199. [CrossRef]

15. Parry, M.L.; Canziani, O.; Palutikof, J.; Van der Linden, P.; Hanson, C. (Eds.) *Climate Change 2007-Impacts, Adaptation and Vulnerability: Working Group II Contribution to the Fourth Assessment Report of the IPCC*; Cambridge University Press: Cambridge, UK, 2007.
16. Liggins, F.; Betts, R.A.; McGuire, B. Projected future climate changes in the context of geological and geomorphological hazards. *Philos. Trans. R. Soc. A* **2010**, *368*, 2347–2367. [CrossRef]
17. Shakhova, N.; Semiletov, I.; Salyuk, A.; Kosmach, D.; Bel'cheva, N. Methane release on the Arctic East Siberian shelf. *Geophys. Res. Abst.* **2007**, *9*, 01071.
18. Shakhova, N.; Semiletov, I.; Salyuk, A.; Kosmach, D. Anomalies of methane in the atmosphere over the East Siberian shelf: Is there any sign of methane leakage from shallow shelf hydrates? EGU General Assembly 2008. *Geophys. Res. Abstr.* **2008**, *10*, 01526.
19. Shakhova, N.; Semiletov, I.; Salyuk, A.; Vusupov, V.; Kosmach, D.; Gustafsson, O. Extensive methane venting to the atmosphere from sediments of the East Siberian Arctic Shelf. *Science* **2010**, *327*, 1246–1250. [CrossRef]
20. Clennell, M.B.; Hovland, M.; Booth, J.S.; Henry, P.; Winters, W.J. Formation of natural gas hydrates in marine sediments 1. Conceptual model of gas hydrate growth conditioned by host sediment properties. *J. Geophys. Res.* **1999**, *104*, 22985–23003. [CrossRef]
21. Henry, P.; Thomas, M.; Clennell, M.B. Formation of natural gas hydrates in marine sediments. 2. Thermodynamic calculations of stability conditions in porous sediments. *J. Geophys. Res.* **1999**, *104*, 23005–23022. [CrossRef]
22. Archer, D. Methane hydrate stability and anthropogenic climate change. *Biogeosciences* **2007**, *4*, 521–544. [CrossRef]
23. Archer, D.; Buffett, B.; Brovkin, V. Ocean methane hydrates as a slow tipping point in the global carbon cycle. *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 20596–20601. [CrossRef]
24. Gough, C.; Mander, S.; Haszeldine, S. A roadmap for carbon capture and storage in the UK. *Int. J. Greenh. Gas Control* **2010**, *4*, 1–12. [CrossRef]
25. D'Alessandro, D.M.; Smit, B.; Long, J.R. Carbon dioxide capture: Prospects for new materials. *Angew. Chem. Int. Ed.* **2010**, *49*, 6058–6082. [CrossRef]
26. Aaron, D.; Tsouris, C. Separation of CO_2 from Flue Gas: A Review. *Sep. Sci. Technol.* **2005**, *40*, 321–348. [CrossRef]
27. Constable, S.; Stern, L.A. Monitoring Offshore CO_2 Sequestration Using Marine CSEM Methods; Constraints Inferred from Field- and Laboratory-Based Gas Hydrate Studies. *Energies* **2022**, *15*, 7411. [CrossRef]
28. Glew, D.N.; Rath, N.S. Variable composition of chlorine and ethylene oxide clathrate hydrates. *J. Chem. Phys.* **1966**, *44*, 1710. [CrossRef]
29. Happel, J. New vistas for gas hydrate research and technology. *Int. Conf. Nat. Gas Hydrates* **1994**, *715*, 564–569. [CrossRef]
30. Spencer, B.F. Civil engineering applications of smart damping technology. In Proceedings of the 5th International Conference on Vibration Engineering, Nanjing, China, 18–20 September 2002; pp. 771–782.
31. Linga, P.; Adeyemo, A.; Englezos, P. Medium-pressure clathrate hydrate/membrane hybrid process for postcombustion capture of carbon dioxide. *Environ. Sci. Technol.* **2008**, *42*, 315–320. [CrossRef]
32. Kang, S.P.; Lee, H.; Lee, C.S.; Sung, W.M. Hydrate phase equilibria of the guest mixtures containing CO_2, N_2 and tetrahydrofuran. *Fluid Phase Equilib.* **2001**, *185*, 101–109. [CrossRef]
33. Kvenvolden, K.A. Potential effects of gas hydrate on human welfare. *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 3420–3426. [CrossRef]
34. Koh, D.Y.; Kang, H.; Lee, J.W.; Park, Y.; Kim, S.J.; Lee, J.; Lee, J.Y.; Lee, H. Energy-efficient natural gas hydrate production using gas exchange. *Appl. Energy* **2016**, *162*, 114–130. [CrossRef]
35. Wang, X.H.; Li, F.G.; Xu, Y.X.; Sun, C.Y.; Pan, H.; Liu, B.; Yang, L.Y.; Chen, G.J.; Li, Q.P. Elastic properties of hydrate-bearing sandy sediment during CH_4–CO_2 replacement. *Energy Convers. Manag.* **2015**, *99*, 274–281. [CrossRef]
36. Ersland, G.; Husebø, J.; Graue, A.; Baldwin, B.A.; Howard, J.; Stevens, J. Measuring gas hydrate formation and exchange with CO_2 in Bentheim sandstone using MRI tomography. *Chem. Eng. J.* **2010**, *158*, 25–31. [CrossRef]
37. Lee, H.; Seo, Y.; Seo, Y.T.; Moudrakovski, I.L.; Ripmeester, J.A. Recovering methane from solid methane hydrate with carbon dioxide. *Angew. Chem. Int. Ed.* **2003**, *42*, 5048–5051. [CrossRef]
38. Xu, C.G.; Cai, J.; Lin, F.H.; Chen, Z.Y.; Li, X.S. Raman analysis on methane production from natural gas hydrate by carbon dioxide–methane replacement. *Energy* **2015**, *79*, 111–116. [CrossRef]
39. Baldwin, B.A.; Stevens, J.; Howard, J.J.; Graue, A.; Kvamme, B.; Aspenes, E.; Ersland, G.; Husebø, J.; Zornes, D.R. Using magnetic resonance imaging to monitor CH_4 hydrate formation and spontaneous conversion of CH_4 hydrate to CO_2 hydrate in porous media. *Magn. Reson. Imaging* **2009**, *27*, 720–726. [CrossRef]
40. Ota, M.; Morohashi, K.; Abe, Y.; Watanabe, M.; Smith, J.R.L.; Inomata, H. Replacement of CH_4 in the hydrate by use of liquid CO_2. *Energy Convers. Manag.* **2005**, *46*, 1680–1691. [CrossRef]
41. Park, Y.; Kim, D.Y.; Lee, J.W.; Huh, D.G.; Park, K.P.; Lee, J.; Lee, H. Sequestering carbon dioxide into complex structures of naturally occurring gas hydrates. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 12690–12694. [CrossRef]
42. Cha, M.; Shin, K.; Lee, H.; Moudrakovski, I.L.; Ripmeester, J.A.; Seo, Y. Kinetics of methane hydrate replacement with carbon dioxide and nitrogen gas mixture using in situ NMR spectroscopy. *Environ. Sci. Technol.* **2015**, *49*, 1964–1971. [CrossRef]
43. Lee, Y.; Kim, Y.; Lee, J.; Lee, H.; Seo, Y. CH_4 recovery and CO_2 sequestration using flue gas in natural gas hydrates as revealed by a micro-differential scanning calorimeter. *Appl. Energy* **2015**, *150*, 120–127. [CrossRef]
44. Lee, B.R.; Koh, C.A.; Sum, A.K. Quantitative measurement and mechanisms for CH_4 production from hydrates with the injection of liquid CO_2. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14922–14927. [CrossRef]

45. Anderson, B.; Boswell, R.; Collett, T.S.; Farrell, H.; Ohtsuki, S.; White, M.; Zyrianova, M. Review of the findings of the Ignik Sikumi CO_2-CH_4 gas hydrate exchange field trial. In Proceedings of the 8th International Conference on Gas Hydrates, Bejing, China, 28 July–1 August 2014.
46. Zhang, L.; Yang, L.; Wang, J.; Zhao, J.; Dong, H.; Yang, M.; Liu, Y.; Song, Y. Enhanced CH_4 recovery and CO_2 storage via thermal stimulation in the CH_4/CO_2 replacement of methane hydrate. *Chem. Eng. J.* **2017**, *308*, 40–49. [CrossRef]
47. Shin, K.; Park, Y.; Cha, M.; Park, K.P.; Huh, D.G.; Lee, J.; Kim, S.J.; Lee, H. Swapping phenomena occurring in deep-sea gas hydrates. *Energy Fuels* **2008**, *22*, 3160–3163. [CrossRef]
48. Lee, Y.; Kim, Y.; Seo, Y. Enhanced CH_4 recovery induced via structural transformation in the CH_4/CO_2 replacement that occurs in sH hydrates. *Environ. Sci. Technol.* **2015**, *49*, 8899–8906. [CrossRef]
49. Chibura, P.E.; Zhang, W.; Luo, A.; Wang, J. A review on gas hydrate production feasibility for permafrost and marine hydrates. *J. Nat. Gas Sci. Eng.* **2022**, *100*, 104441. [CrossRef]
50. Chong, Z.R.; Yang, S.H.B.; Babu, P.; Linga, P.; Li, X.S. Review of natural gas hydrates as an energy resource: Prospects and challenges. *Appl. Energy* **2016**, *162*, 1633–1652. [CrossRef]
51. Sun, J.; Hao, X.; Li, C.; Wu, N.; Chen, Q.; Liu, C.; Li, Y.; Meng, Q.; Huang, L.; Bu, Q. Experimental Study on the Distribution Characteristics of CO_2 in Methane Hydrate-Bearing Sediment during CH_4/CO_2 Replacement. *Energies* **2022**, *15*, 5634. [CrossRef]
52. Cai, W.; Huang, X.; Lu, H. Instrumental Methods for Cage Occupancy Estimation of Gas Hydrate. *Energies* **2022**, *15*, 485. [CrossRef]
53. Gajanayake, S.M.; Gamage, R.P.; Li, X.S.; Huppert, H. Natural gas hydrates—Insights into a paradigm-shifting energy resource. *Energy Rev.* **2023**, *2*, 100013. [CrossRef]
54. Gajanayake, S.; Gamage, R.P.; Wanniarachchige, P.; Zhang, D. Quantification of CO_2 replacement in methane gas hydrates: A molecular dynamics perspective. *J. Nat. Gas Sci. Eng.* **2022**, *98*, 104396. [CrossRef]
55. Fan, S.; Yu, W.; Yu, C.; Wang, Y.; Lang, X.; Wang, S.; Li, G.; Huang, H. Investigation of enhanced exploitation of natural gas hydrate and CO_2 sequestration combined gradual heat stimulation with CO_2 replacement in sediments. *J. Nat. Gas Sci. Eng.* **2022**, *104*, 104686. [CrossRef]
56. Li, Q.; Li, S.; Ding, S.; Yin, Z.; Liu, L.; Li, S. Numerical Simulation of Gas Production and Reservoir Stability during CO_2 Exchange in Natural Gas Hydrate Reservoir. *Energies* **2022**, *15*, 8968. [CrossRef]
57. Tian, H.; Yu, Z.; Xu, T.; Xiao, T.; Shang, S. Evaluating the recovery potential of CH_4 by injecting CO_2 mixture into marine hydrate-bearing reservoirs with a new multi-gas hydrate simulator. *J. Clean. Prod.* **2022**, *361*, 132270. [CrossRef]
58. Pandey, G.; Poothia, T.; Kumar, A. Hydrate based carbon capture and sequestration (HBCCS): An innovative approach towards decarbonization. *Appl. Energy* **2022**, *326*, 119900. [CrossRef]
59. Bian, J.; Wang, H.; Yang, K.; Chen, J.; Cao, X. Spatial differences in pressure and heat transfer characteristics of CO_2 hydrate with dissociation for geological CO_2 storage. *Energy* **2022**, *240*, 122508. [CrossRef]
60. Bajpai, S.; Shreyash, N.; Singh, S.; Memon, A.R.; Sonker, M.; Tiwary, S.K.; Biswas, S. Opportunities, challenges and the way ahead for carbon capture, utilization and sequestration (CCUS) by the hydrocarbon industry: Towards a sustainable future. *Energy Rep.* **2022**, *8*, 15595–15616. [CrossRef]
61. Xie, Y.; Zhu, Y.J.; Zheng, T.; Yuan, Q.; Sun, C.Y.; Yang, L.Y.; Chen, G.J. Replacement in CH_4-CO_2 hydrate below freezing point based on abnormal self-preservation differences of CH_4 hydrate. *Chem. Eng. J.* **2021**, *403*, 126283. [CrossRef]
62. Lee, Y.; Choi, W.; Shin, K.; Seo, Y. CH_4-CO_2 replacement occurring in sII natural gas hydrates for CH_4 recovery and CO_2 sequestration. *Energy Convers. Manag.* **2017**, *150*, 356–364. [CrossRef]
63. Ndlovu, P.; Babaee, S.; Naidoo, P. Review on CH_4-CO_2 replacement for CO_2 sequestration and CH_4/CO_2 hydrate formation in porous media. *Fuel* **2022**, *320*, 123795. [CrossRef]
64. Choi, W.; Mok, J.; Lee, J.; Lee, Y.; Lee, J.; Sum, A.K.; Seo, Y. Effective CH_4 production and novel CO_2 storage through depressurization-assisted replacement in natural gas hydrate-bearing sediment. *Appl. Energy* **2022**, *326*, 119971. [CrossRef]
65. Bruant, R.; Guswa, A.; Celia, M.; Peters, C. Safe storage of CO_2 in deep saline aquifers. *Environ. Sci.* **2002**, *36*, 240A–245A. [CrossRef]
66. Cui, Y.; Lu, C.; Wu, M.; Peng, Y.; Yao, Y.; Luo, W. Review of exploration and production technology of natural gas hydrate. *Adv. Geo-Energy Res.* **2018**, *2*, 53–62. [CrossRef]
67. Manakov, A.Y.; Stoporev, A.S. Physical chemistry and technological applications of gas hydrates: Topica aspects. *Russ. Chem. Rev.* **2021**, *90*, 566. [CrossRef]
68. Yan, C.; Li, Y.; Cheng, Y.; Wei, J.; Tian, W.; Li, S.; Wang, Z. Multifield coupling mechanism in formations around a wellbore during the exploitation of methane hydrate with CO_2 replacement. *Energy* **2022**, *245*, 123283. [CrossRef]
69. Wei, W.N.; Li, B.; Gan, Q.; Li, Y.L. Research progress of natural gas hydrate exploitation with CO_2 replacement: A review. *Fuel* **2022**, *312*, 122873. [CrossRef]
70. Sun, Y.F.; Cao, B.J.; Zhong, J.R.; Kan, J.Y.; Li, R.; Niu, J.S.; Chen, H.N.; Chen, G.J.; Wu, G.Z.; Sun, C.Y.; et al. Gas production from unsealed hydrate-bearing sediments after reservoir reformation in a large-scale simulator. *Fuel* **2022**, *308*, 121957. [CrossRef]
71. Giovannetti, R.; Gambelli, A.M.; Rossi, A.; Castellani, B.; Minicucci, M.; Zannotti, M.; Nicolini, A.; Rossi, F. Thermodynamic assessment and microscale Raman spectroscopy of binary CO_2/CH_4 hydrates produced during replacement applications in natural reservoirs. *J. Mol. Liq.* **2022**, *368*, 120739. [CrossRef]

72. Nizami, M.; Nugroho, R.I.; Milati, K.H.; Pratama, Y.W.; Purwanto, W.W. Process and levelized cost assessment of high CO_2-content natural gas for LNG production using membrane and CFZ CO_2 separation integrated with CO_2 sequestration. *Sustain. Energy Technol. Assess.* **2022**, *49*, 101744. [CrossRef]
73. Li, B.; Xu, T.; Zhang, G.; Guo, W.; Liu, H.; Wang, Q.; Qu, L.; Sun, Y. An experimental study on gas production from fracture-filled hydrate by CO_2 and CO_2/N_2 replacement. *Energy Convers. Manag.* **2018**, *165*, 738–747. [CrossRef]
74. Wang, Y.; Feng, J.C.; Li, X.S.; Zhan, L.; Li, X.Y. Pilot-scale experimental evaluation of gas recovery from methane hydrate using cycling depressurization scheme. *Energy* **2018**, *160*, 835–844. [CrossRef]
75. Li, B.; Liu, S.D.; Liang, Y.P.; Liu, H. The use of electrical heating for the enhancement of gas recovery from methane hydrate in porous media. *Appl. Energy* **2018**, *227*, 694–702. [CrossRef]
76. Wang, P.; Teng, Y.; Zhu, J.; Bao, W.; Han, S.; Li, Y.; Zhao, Y.; Xie, H. Review on the synergistic effect between metal–organic frameworks and gas hydrates for CH_4 storage and CO_2 separation applications. *Renew. Sustain. Energy Rev.* **2022**, *167*, 112807. [CrossRef]
77. Pandey, J.S.; von Solms, N. Metal–organic frameworks and gas hydrate synergy: A pandora's box of unanswered questions and revelations. *Energies* **2023**, *16*, 111. [CrossRef]
78. Rossi, F.; Gambelli, A.M.; Sharma, D.K.; Castellani, B.; Nicolini, A.; Castaldi, M.J. Experiments on methane hydrates formation in seabed deposits and gas recovery adopting carbon dioxide replacement strategies. *Appl. Therm. Eng.* **2019**, *148*, 371–381. [CrossRef]
79. Sun, Y.F.; Zhong, J.R.; Li, R.; Zhu, T.; Cao, X.Y.; Chen, G.J.; Wang, X.H.; Yang, L.Y.; Sun, C.Y. Natural gas hydrate exploitation by CO_2/H_2 continuous Injection—Production mode. *Appl. Energy* **2018**, *226*, 10–21. [CrossRef]
80. Cao, B.J.; Sun, Y.F.; Chen, H.N.; Zhong, J.R.; Wang, M.L.; Niu, M.Y.; Kan, J.Y.; Sun, C.Y.; Chen, D.Y.; Chen, G.J. An approach to the high efficient exploitation of nature gas hydrate and carbon sequestration via injecting CO_2/H_2 gas mixture with varying composition. *Chem. Eng. J.* **2023**, *455*, 140634. [CrossRef]
81. Xie, Y.; Zhu, Y.J.; Cheng, L.W.; Zheng, T.; Zhong, J.R.; Xiao, P.; Sun, C.Y.; Chen, G.J.; Feng, J.C. The coexistence of multiple hydrates triggered by varied H2 molecule occupancy during CO_2/H_2 hydrate dissociation. *Energy* **2023**, *262*, 125461. [CrossRef]
82. Wang, X.H.; Sun, Y.F.; Wang, Y.F.; Li, N.; Sun, C.Y.; Chen, G.J.; Liu, B.; Yang, L.Y. Gas production from hydrates by CH_4-CO_2/H_2 replacement. *Appl. Energy* **2017**, *188*, 305–314. [CrossRef]
83. Kang, S.P.; Lee, H. Recovery of CO_2 from flue gas using gas hydrate: Thermodynamic verification through phase equilibrium measurements. *Environ. Sci. Technol.* **2000**, *34*, 4397–4400. [CrossRef]
84. Linga, P.; Kumar, R.; Englezos, P. The clathrate hydrate process for post and pre-combustion capture of carbon dioxide. *J. Hazard. Mater.* **2007**, *149*, 625–629. [CrossRef]
85. Seo, Y.T.; Moudrakovski, I.L.; Ripmeester, J.A.; Lee, J.W.; Lee, H. Efficient Recovery of CO_2 from Flue Gas by Clathrate Hydrate Formation in Porous Silica Gels. *Environ. Sci. Technol.* **2005**, *39*, 2315–2319. [CrossRef]
86. Linga, P.; Kumar, R.; Englezos, P. Gas hydrate formation from hydrogen/carbon dioxide and nitrogen/carbon dioxide gas mixtures. *Chem. Eng. Sci.* **2007**, *62*, 4268–4276. [CrossRef]
87. Li, W.; Xu, H.; Ma, X.; Dong, Z.; Lei, G.; Qian, S.; Wei, X.; Pan, X. Molecular dynamics-based analysis of the factors influencing the CO_2 replacement of methane hydrate. *J. Mol. Graph. Model.* **2023**, *119*, 108394. [CrossRef]
88. Meng, Z.; Xu, J.; Hao, Y.; Chen, J.; Wang, B.; Zhang, X.; Zhang, J. Molecular study on the behavior of CO_2 hydrate growth promoted by the electric field. *J. Petrol. Sci. Eng.* **2023**, *221*, 111261. [CrossRef]
89. Zhang, X.; Yang, H.; Huang, T.; Li, J.; Li, P.; Wu, Q.; Wang, Y.; Zhang, P. Research progress of molecular dynamics simulation on the formation-decomposition mechanism and stability of CO_2 hydrate in porous media: A review. *Renew. Sustain. Energy Rev.* **2022**, *167*, 112820. [CrossRef]
90. Lee, Y.; Go, W.; Kim, Y.; Lim, J.; Choi, W.; Seo, Y. Molecular guest exchange and subsequent structural transformation in CH_4–CO_2 replacement occurring in sH hydrates as revealed by ^{13}C NMR spectroscopy and molecular dynamic simulations. *Chem. Eng. J.* **2023**, *455*, 140937. [CrossRef]
91. Guo, Y.; Li, J.; Ahmed, R.; Shen, N.; Li, X. An enthalpy model of CO_2-CH_4-H_2S-N_2-brine systems applied in simulation of non-isothermal multiphase and multi-component flow with high pressure, temperature and salinity. *J. CO_2 Util.* **2019**, *31*, 85–97. [CrossRef]
92. Shagapov, V.S.; Khasanov, M.K.; Musakaev, N.G.; Duong, N.H. Theoretical research of the gas hydrate deposits development using the injection of carbon dioxide. *Int. J. Heat Mass Transf.* **2017**, *107*, 347–357. [CrossRef]
93. Khasanov, M.K.; Rafikova, G.R.; Musakaev, N.G. Mathematical model of carbon dioxide injection into a porous reservoir saturated with methane and its gas hydrate. *Energies* **2020**, *13*, 440. [CrossRef]
94. Khasanov, M.K.; Stolpovsky, M.V.; Gimaltdinov, I.K. Mathematical model of injection of liquid carbon dioxide in a reservoir saturated with methane and its hydrate. *Int. J. Heat Mass Transf.* **2019**, *132*, 529–538. [CrossRef]
95. Khasanov, M.K.; Stolpovsky, M.V.; Gimaltdinov, I.K. Mathematical model for carbon dioxide injection into porous medium saturated with methane and gas hydrate. *Int. J. Heat Mass Transf.* **2018**, *127*, 21–28. [CrossRef]
96. Adamova, T.P.; Skiba, S.S.; Manakov, A.Y.; Misyura, S.Y. Growth rate of CO_2 hydrate film on water–oil and water–gaseous CO_2 interface. *Chin. J. Chem. Eng.* **2002**, *237*, 383–387. [CrossRef]
97. Vlasov, V.A. Diffusion-kinetic model of gas hydrate film growth along the gas–water interface. *Heat Mass Transf.* **2019**, *55*, 3537–3545. [CrossRef]

98. Musakaev, N.G.; Borodin, S.L.; Gubaidullin, A.A. Methodology for the numerical study of the methane hydrate formation during gas injection into a porous medium. *Lobachevskii J. Math.* **2020**, *41*, 1272–1277. [CrossRef]
99. Zhang, X.; Zhang, S.; Yin, S.; He, G.; Li, J.; Wu, Q. Research progress of the kinetics on natural gas hydrate replacement by CO_2-containing mixed gas: A review. *J. Nat. Gas Sci. Eng.* **2022**, *108*, 104837. [CrossRef]
100. Wang, T.; Sun, L.; Fan, Z.; Wei, R.; Li, Q.; Yao, H.; Dong, H.; Zhang, L.; Yang, L.; Zhao, J.; et al. Promoting CH_4/CO_2 replacement from hydrate with warm brine injection for synergistic energy harvest and carbon sequestration. *Chem. Eng. J.* **2023**, *457*, 141129. [CrossRef]
101. Tang, J.; Zeng, D.; Wang, C.; Chen, Y.; He, L.; Cai, N. Study on the influence of SDS and THF on hydrate-based gas separation performance. *Chem. Eng. Res. Des.* **2013**, *91*, 1777–1782. [CrossRef]
102. Oyama, H.; Shimada, W.; Ebinuma, T.; Kamata, Y.; Takeya, S.; Uchida, T.; Nagao, J.; Narita, H. Phase diagram, latent heat, and specific heat of TBAB semi-clathrate hydrate crystals. *Fluid Phase Equilib.* **2005**, *234*, 131–135. [CrossRef]
103. Darbouret, M.; Cournil, M.; Herri, J.M. Rheological study of TBAB hydrate slurries as secondary two-phase refrigerants. *Int. J. Refrig.* **2005**, *28*, 663–671. [CrossRef]
104. Li, X.S.; Xia, Z.M.; Chen, Z.Y.; Yan, K.F.; Li, G.; Wu, H.J. Gas Hydrate Formation Process for Capture of Carbon Dioxide from Fuel Gas Mixture. *Ind. Eng. Chem. Res.* **2010**, *49*, 11614–11619. [CrossRef]
105. Li, S.F.; Fan, S.S.; Wang, J.Q.; Lang, X.M.; Liang, D.Q. CO_2 capture from binary mixture via forming hydrate with the help of tetra-n-butyl ammonium bromide. *J. Nat. Gas Chem.* **2009**, *18*, 15–20. [CrossRef]
106. Li, X.S.; Xu, C.G.; Chen, Z.Y.; Wu, H.J. Tetra-n-butyl ammonium bromide semi-clathrate hydrate process for post-combustion capture of carbon dioxide in the presence of dodecyl trimethyl ammonium chloride. *Energy* **2010**, *35*, 3902–3908. [CrossRef]
107. Tan, W.L.; Ahmad, A.L.; Leo, C.P.; Lam, S.S. A critical review to bridge the gaps between carbon capture, storage and use of $CaCO_3$. *J. CO_2 Util.* **2020**, *42*, 101333. [CrossRef]
108. Ahmadloo, F.; Mali, G.; Chapoy, A.; Tohidi, B. Gas Separation and Storage using Semi-Clathrate Hydrates. In Proceedings of the 6th International Conference on Gas Hydrates (ICGH 2008), Vancouver, BC, Canada, 6–10 July 2008.
109. Oyama, H.; Ebinuma, T.; Nagao, J.; Narita, H.; Shimada, W. Phase behavior of TBAB semiclathrate hydrate crystal under several vapor components. In Proceedings of the 6th International Conference on Gas Hydrates (ICGH 2008), Vancouver, BC, Canada, 6–10 July 2008.
110. Fang, K.; Jiang, X.; Wang, C.; Wu, M.; Yan, Y. Properties of the nanoscale hydrophilic cationic pigment based on quaternary surfactant. *J. Dispers. Sci. Technol.* **2008**, *29*, 52–57. [CrossRef]
111. Duc, N.H.; Chauvy, F.; Herri, J.M. CO_2 capture by hydrate crystallization—A potential solution for gas emission of steelmaking industry. *Energy Convers. Manag.* **2007**, *48*, 1313–1322. [CrossRef]
112. Gambelli, A.M.; Presciutti, A.; Rossi, F. Review on the characteristics and advantages related to the use of flue-gas as CO_2/N_2 mixture for gas hydrate production. *Fluid Phase Equilib.* **2021**, *541*, 113077. [CrossRef]
113. Kumar, A.; Bhattacharjee, G.; Kulkarni, B.D.; Kumar, R. Role of surfactants in promoting gas hydrate formation. *Ind. Eng. Chem. Res.* **2015**, *54*, 12217–12232. [CrossRef]
114. Zhang, P.; Wu, Q.; Mu, C.; Chen, X. Nucleation mechanisms of CO_2 hydrate reflected by gas solubility. *Sci. Rep.* **2018**, *8*, 10441–10452. [CrossRef]
115. Molokitina, N.S.; Nesterov, A.N.; Podenko, L.S.; Reshetnikov, A.M. Carbon dioxide hydrate formation with SDS: Further insights into mechanism of gas hydrate growth in the presence of surfactant. *Fuel* **2019**, *235*, 1400–1411. [CrossRef]
116. Lo, C.; Zhang, J.; Somasundaran, P.; Lee, J.W. Investigations of surfactant effects on gas hydrate formation via infrared spectroscopy. *J. Colloid Interface Sci.* **2012**, *376*, 173–176. [CrossRef]
117. Pan, Z.; Wu, Y.; Shang, L.; Zhou, L.; Zhang, Z. Progress in use of surfactant in nearly static conditions in natural gas hydrate formation. *Front. Energy* **2020**, *14*, 463–481. [CrossRef]
118. Tajima, H.; Kiyono, F.; Yamasaki, A. Direct observation of the effect of sodium dodecyl sulfate (SDS) on the gas hydrate formation process in a static mixer. *Energy Fuels* **2010**, *24*, 432–438. [CrossRef]
119. Okutani, K.; Kuwabara, Y.; Mori, Y.H. Surfactant effects on hydrate formation in an unstirred gas/liquid system: Amendments to the previous study using HFC-32 and sodium dodecyl sulfate. *Chem. Eng. Sci.* **2007**, *62*, 3858–3860. [CrossRef]
120. Asaoka, T.; Ikeda, K. Observation of the growth characteristics of gas hydrate in the quiescent-type formation method using surfactant. *J. Cryst. Growth* **2017**, *478*, 1–8. [CrossRef]
121. Zhong, Y.; Rogers, R.E. Surfactant effects on gas hydrate formation. *Chem. Eng. Sci.* **2000**, *55*, 4175–4187. [CrossRef]
122. Irvin, G.; Li, S.; Simmons, B.; John, V.; McPherson, G.; Max, M.; Pellenbarg, R. Control of gas hydrate formation using surfactant systems: Underlying concepts and new applications. *Ann. N. Y. Acad. Sci.* **2000**, *912*, 515–526. [CrossRef]
123. Zhang, B.; Wu, Q.; Sun, D. Effect of surfactant Tween on induction time of gas hydrate formation. *J. China Univ. Min. Technol.* **2008**, *18*, 18–21. [CrossRef]
124. Wang, X.; Zhang, F.; Lipiński, W. Research progress and challenges in hydrate-based carbon dioxide capture applications. *Appl. Energy* **2020**, *269*, 114928. [CrossRef]
125. Lee, Y.J.; Taro, K.; Yoshitaka, Y.; Yoon, J.H. Phase Equilibrium Studies of Tetrahydrofuran (THF) + CH_4, THF + CO_2, CH_4 + CO_2, and THF + CO_2 + CH_4 Hydrates. *J. Chem. Eng. Data* **2012**, *57*, 3543–3548. [CrossRef]
126. Lino, K.; Takeya, S.; Ohmura, R. Characterization of clathrate hydrates formed with CH_4 or CO_2 plus tetrahydropyran. *Fuel* **2014**, *122*, 270–276. [CrossRef]

127. Wang, X.; Zhang, F.; Lipiński, W. Carbon dioxide hydrates for cold thermal energy storage: A review. *Sol. Energy* **2020**, *211*, 11–30. [CrossRef]
128. Mooijer-van den Heuvel, M.M.; Witteman, R.; Peters, C.J. Phase behaviour of gas hydrates of carbon dioxide in the presence of tetrahydropyran, cyclobutanone, cyclohexane and methylcyclohexane. *Fluid Phase Equilib.* **2001**, *182*, 97–110. [CrossRef]
129. Yu, Y.S.; Zhang, Q.Z.; Li, X.S.; Chen, C.; Zhou, S.D. Kinetics, compositions and structures of carbon dioxide/hydrogen hydrate formation in the presence of cyclopentane. *Appl. Energy* **2020**, *265*, 114808. [CrossRef]
130. Hong, S.; Moon, S.; Lee, Y.; Lee, S.; Park, Y. Investigation of thermodynamic and kinetic effects of cyclopentane derivatives on CO_2 hydrates for potential application to seawater desalination. *Chem. Eng. J.* **2019**, *363*, 99–106. [CrossRef]
131. Pahlavanzadeh, H.; Mohammadi, A.H.; Jokandan, B.A.; Farhoudi, A. Clathrate hydrate formation of CO_2 in the presence of water miscible (1,4-dioxane) and partially water miscible (cyclopentane) organic compounds: Experimental measurement and thermodynamic modeling. *J. Petrol. Sci. Eng.* **2019**, *179*, 465–473. [CrossRef]
132. Torré, J.P.; Haillot, D.; Rigal, S.; de Souza Lima, R.; Dicharry, C.; Bedecarrats, J.P. 1,3 Dioxolane versus tetrahydrofuran as promoters for CO_2-hydrate formation: Thermodynamics properties, and kinetics in presence of sodium dodecyl sulfate. *Chem. Eng. Sci.* **2015**, *126*, 688–697. [CrossRef]
133. Tang, M.; Wang, H.W.; Wu, Y.P.; Tsai, J.C.; Chen, Y.P. Experimental Measurements for Equilibrium Conditions of Carbon Dioxide Hydrate Mixtures with Each Additive of 1,3-Dioxane, Acetamide, Cyclopentanol, Cyclopentanone, or 1,3,5-Trioxane. *J. Chem. Eng. Data* **2022**, *67*, 2954–2962. [CrossRef]
134. Babu, P.; Datta, S.; Kumar, R.; Linga, P. Impact of experimental pressure and temperature on semiclathrate hydrate formation for pre-combustion capture of CO_2 using tetra-n-butyl ammonium nitrate. *Energy* **2014**, *78*, 458–464. [CrossRef]
135. Zhang, P.; Ye, N.; Zhu, H.; Xiao, X. Hydrate Equilibrium Conditions of Tetra-n-butylphosphonium Bromide + Carbon Dioxide and the Crystal Morphologies. *J. Chem. Eng. Data* **2013**, *58*, 1781–1786. [CrossRef]
136. Deng, X.Y.; Deng, X.Y.; Deng, X.Y.; Yang, Y.; Zhong, D.L.; Li, X.Y.; Ge, B.B.; Yan, J. New Insights into the Kinetics and Morphology of CO_2 Hydrate Formation in the Presence of Sodium Dodecyl Sulfate. *Energy Fuels* **2021**, *35*, 13877–13888. [CrossRef]
137. Kumar, A.; Sakpal, T.; Linga, P.; Kumar, R. Influence of contact medium and surfactants on carbon dioxide clathrate hydrate kinetics. *Fuel* **2013**, *105*, 664–671. [CrossRef]
138. Sinehbaghizadeh, S.; Saptoro, A.; Mohammadi, A.H. CO_2 hydrate properties and applications: A state of the art. *Prog. Energy Combust. Sci.* **2022**, *93*, 101026. [CrossRef]
139. Ndlovu, P.; Babaee, S.; Naidoo, P. Experimental Study of CH_4-CO_2 Replacement in Gas Hydrates in the presence of nitrogen and graphene nanoplatelets. *J. Mol. Liq.* **2023**, *371*, 121109. [CrossRef]
140. Wu, W.; Hao, B.; Guo, Y.; Yang, J.; Du, M.; Zheng, Q.; Bai, Z. Application of monocyclic compounds as natural gas hydrate promoters: A review. *Chem. Eng. Res. Des.* **2023**, *190*, 66–90. [CrossRef]
141. Deng, Z.; Fan, S.; Wang, Y.; Lang, X.; Li, G.; Liu, F.; Li, M. High storage capacity and high formation rate of carbon dioxide hydrates via super-hydrophobic fluorinated graphenes. *Energy* **2023**, *264*, 126045. [CrossRef]
142. Tee, P.F.; Abdullah, M.O.; Tan, I.A.W.; Rashid, N.K.A.; Amin, M.A.M.; Nolasco-Hipolito, C.; Bujang, K. Review on hybrid energy systems for wastewater treatment and bio-energy production. *Renew. Sustain. Energy Rev.* **2016**, *54*, 235–246. [CrossRef]
143. Gonçalves, A.L.; Pires, J.C.M.; Simões, M. A review on the use of microalgal consortia for wastewater treatment. *Algal Res.* **2017**, *24*, 403–415. [CrossRef]
144. Azetsu-Scott, K.; Yeats, P.; Wohlgeschaffen, G.; Dalziel, J.; Niven, S.; Lee, K. Precipitation of heavy metals in produced water: Influence on contaminant transport and toxicity. *Mar. Environ. Res.* **2007**, *63*, 146–167. [CrossRef]
145. Xu, P.; Zeng, G.M.; Huang, D.L.; Feng, C.L.; Hu, S.; Zhao, M.H.; Liu, Z.F. Use of iron oxide nanomaterials in wastewater treatment: A review. *Sci. Total Environ.* **2012**, *424*, 1–10. [CrossRef]
146. Srivastava, N.K.; Majumder, C.B. Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. *J. Hazard. Mater.* **2008**, *151*, 1–8. [CrossRef]
147. Shrestha, R.; Ban, S.; Devkota, S.; Sharma, S.; Joshi, R.; Tiwari, A.P.; Joshi, M.K. Technological trends in heavy metals removal from industrial wastewater: A review. *J. Environ. Chem. Eng.* **2021**, *9*, 105688. [CrossRef]
148. Sharma, A.; Mangla, D.; Shehnaz; Chaudhry, S.A. Recent advances in magnetic composites as adsorbents for wastewater remediation. *J. Environ. Manag.* **2022**, *306*, 114483. [CrossRef]
149. Quero, G.M.; Cassin, D.; Botter, M.; Perini, L.; Luna, G.M. Patterns of benthic bacterial diversity in coastal areas contaminated by heavy metals, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). *Front. Microb.* **2015**, *6*, 1053. [CrossRef]
150. Gupta, V.K.; Suhas. Application of low-cost adsorbents for dye removal—A review. *J. Environ. Manag.* **2009**, *90*, 2313–2342. [CrossRef]
151. Finizio, A.; Azimonti, G.; Villa, S. Occurrence of pesticides in surface water bodies: A critical analysis of the Italian national pesticide survey programs. *J. Environ. Monit.* **2011**, *13*, 49–57. [CrossRef]
152. Ngah, W.S.W.; Teong, L.C.; Hanafiah, M.A.K.M. Adsorption of dyes and heavy metal ions by chitosan composites: A review. *Carbohydr. Polym.* **2011**, *83*, 1446–1456. [CrossRef]
153. Khan, N.A.; Ahmed, S.; Farooqi, I.H.; Ali, I.; Vambol, V.; Changani, F.; Khan, A.H. Occurrence, sources and conventional treatment techniques for various antibiotics present in hospital wastewaters: A critical review. *TrAC Trends Anal. Chem.* **2020**, *129*, 115921. [CrossRef]

154. Buchanan, B.B. Removing Salt from Sea Water. U.S. Patent No. 3,027,320, 27 March 1962.
155. Walton, P.R. Continuous Saline Water Purification. U.S. Patent No. 3,132,096, 5 May 1964.
156. Klass, D. Hydrate Forming in Water Desalination. U.S. Patent No. 3,856,492, 24 December 1974.
157. McCormack, R.A. Clathrate Freeze Desalination Apparatus and Method. U.S. Patent No. 5,553,456, 10 September 1996.
158. Max, M.D.; Pellenbarg, R.E. Desalination through Methane Hydrate. U.S. Patent No. 5,873,262, 23 February 1999.
159. Heinemann, R.F.; Huang, D.D.T.; Long, J.; Saeger, R.B. Process for Making Gas Hydrates. U.S. Patent No. 6,028,234, 22 February 2000.
160. Max, M.D.; Korsgaard, J. Hydrate-Based Desalination with Hydrate-Elevating Density-Driven Circulation. U.S. Patent No. 6,969,467, 10 November 2005.
161. Simmons, B.A.; Bradshaw, R.W.; Dedrick, D.E.; Anderson, D.W. Complex Admixtures of Clathrate Hydrates in a Water Desalination Method. U.S. Patent No. 7560028B1, 14 July 2009.
162. Phelps, T.J.; Tsouris, C.; Palumbo, A.V.; Riestenberg, D.E.; McCallum, S.D. Method for Excluding Salt and Other Soluble Materials from ProducedWater. U.S. Patent No. 7,569,737, 4 August 2009.
163. Katyal, A.A. System and Method for Hydrate-Based Desalination. U.S. Patent No. 9,643,860, 9 May 2017.
164. Parker, A. Potable water from sea-water. *Nature* **1942**, *149*, 184–186. [CrossRef]
165. Aghigh, A.; Alizadeh, V.; Wong, H.Y.; Islam, M.S.; Amin, N.; Zaman, M. Recent advances in utilization of graphene for filtration and desalination of water: A review. *Desalination* **2015**, *365*, 389–397. [CrossRef]
166. Sahu, P. Clathrate hydrate technology for water reclamation: Present status and future prospects. *J. Water Process Eng.* **2021**, *41*, 102058. [CrossRef]
167. Zhang, J.; Chen, S.; Mao, N.; He, T. Progress and prospect of hydrate-based desalination technology. *Front. Energy* **2022**, *16*, 445–459. [CrossRef]
168. Nallakukkala, S.; Rehman, A.; Zaini, D.B.; Lal, B. Gas hydrate-based heavy metal ion removal from industrial wastewater: A review. *Water* **2022**, *14*, 1171. [CrossRef]
169. Montazeri, S.M.; Kolliopoulos, G. Hydrate based desalination for sustainable water treatment: A review. *Desalination* **2022**, *537*, 115855. [CrossRef]
170. Chong, Z.R.; He, T.; Babu, P.; Zheng, J.; Linga, P. Economic evaluation of energy efficient hydrate-based desalination utilizing cold energy from liquefied natural gas (LNG). *Desalination* **2019**, *463*, 69–80. [CrossRef]
171. He, T.; Chong, Z.R.; Zheng, J.; Ju, Y.; Linga, P. LNG cold energy utilization: Prospects and challenges. *Energy* **2019**, *170*, 557–568. [CrossRef]
172. Zheng, J.; Yang, M. Experimental investigation on novel desalination system via gas hydrate. *Desalination* **2020**, *478*, 114284. [CrossRef]
173. Sarshar, M.; Sharafi, A.H. Simultaneous water desalination and CO_2 capturing by hydrate formation. *Water Treat.* **2011**, *28*, 59–64. [CrossRef]
174. Park, K.; Hong, S.Y.; Lee, J.W.; Kang, K.C.; Lee, Y.C.; Ha, M.G.; Lee, J.D. A new apparatus for seawater desalination by gas hydrate process and removal characteristics of dissolved minerals (Na^+, Mg^{2+}, Ca^{2+}, K^+, B^{3+}). *Desalination* **2011**, *274*, 91–96. [CrossRef]
175. Cha, J.H.; Seol, Y. Increasing gas hydrate formation temperature for desalination of high salinity produced water with secondary guests. *ACS Sustain. Chem. Eng.* **2013**, *1*, 1218–1224. [CrossRef]
176. Yang, M.; Zheng, J.; Liu, W.; Liu, Y.; Song, Y. Effects of C_3H_8 on hydrate formation and dissociation for integrated CO_2 capture and desalination technology. *Energy* **2015**, *93*, 1971–1979. [CrossRef]
177. Yang, M.; Song, Y.; Jiang, L.; Liu, W.; Dou, B.; Jing, W. Effects of operating mode and pressure on hydrate-based desalination and CO_2 capture in porous media. *Appl. Energy* **2014**, *135*, 504–511. [CrossRef]
178. Sun, S.C.; Liu, C.L.; Ye, Y.G. Phase equilibrium condition of marine carbon dioxide hydrate. *J. Chem. Thermodyn.* **2013**, *57*, 256–260. [CrossRef]
179. Yang, M.; Song, Y.; Liu, Y.; Lam, W.H.; Li, Q. Equilibrium conditions for CO_2 hydrate in porous medium. *J. Chem. Thermodyn.* **2011**, *43*, 334–338. [CrossRef]
180. Zheng, J.; Yang, M.; Liu, Y.; Wang, D.; Song, Y. Effects of cyclopentane on CO_2 hydrate formation and dissociation as a co-guest molecule for desalination. *J. Chem. Thermodyn.* **2017**, *104*, 9–15. [CrossRef]
181. Koh, C.A.; Wisbey, R.P.; Wu, X.; Westacott, R.E. Water ordering around methane during hydrate formation. *J. Chem. Phys.* **2000**, *113*, 6390–6397. [CrossRef]
182. Wu, Y.; He, Y.; Tang, T.; Zhai, M. Molecular dynamic simulations of methane hydrate formation between solid surfaces: Implications for methane storage. *Energy* **2023**, *262*, 12551. [CrossRef]
183. Nakate, P.; Ghosh, B.; Das, S.; Roy, S.; Kumar, R. Molecular dynamics study on growth of carbon dioxide and methane hydrate from a seed crystal. *Chin. J. Chem. Eng.* **2019**, *27*, 2074–2080. [CrossRef]
184. Tung, Y.T.; Chen, L.J.; Chen, Y.P.; Lin, S.T. The growth of structure I methane hydrate from molecular dynamics simulations. *J. Phys. Chem. B* **2010**, *114*, 10804–10813. [CrossRef]
185. English, N.J.; MacElroy, J.M.D. Perspectives on molecular simulation of clathrate hydrates: Progress, prospects and challenges. *Chem. Eng. Sci.* **2015**, *121*, 133–156. [CrossRef]
186. Bai, D.; Zhang, X.; Chen, G.; Wang, W. Replacement mechanism of methane hydrate with carbon dioxide from microsecond molecular dynamics simulations. *Energy Environ. Sci.* **2012**, *5*, 7033–7041. [CrossRef]

187. Liu, N.; Zhou, J.; Hong, C. Molecular dynamics simulations on dissociation of CO_2 hydrate in the presence of inhibitor. *Chem. Phys.* **2020**, *538*, 110894. [CrossRef]
188. Nallakukkala, S.; Lal, B.; Shariff, M.A. Influence of water volume on CO_2 hydrate-based desalination of brine solution. *Mater. Today Proc.* **2022**, *56*, 2172–2177. [CrossRef]
189. Rehman, A.N.; Lal, B.; Pendyala, R.; Yusoff, M.H.M. Unusual CO_2 hydrate formation in porous media: Implications on geo-CO_2 storage laboratory testing methods. *Mater. Today Proc.* **2022**, *57*, 1363–1368. [CrossRef]
190. Falahieh, M.M.; Bonyadi, M.; Lashanizadegan, A. A new hybrid desalination method based on the CO_2 gas hydrate and capacitive deionization processes. *Desalination* **2021**, *502*, 114932. [CrossRef]
191. Gautam, R.; Kumar, S.; Sahai, M.; Kumar, A. Solid CO_2 hydrates for sustainable environment: Application in carbon capture and desalination. *Mater. Today Proc.* **2022**, *67*, 609–615. [CrossRef]
192. Franks, F. *Water. A Comprehensive Treatise*; Plenum Press: New York, NY, USA, 1975.
193. Ahuja, A.; Zylyftari, G.; Morris, J.F. Yield stress measurements of cyclopentane hydrate slurry. *J. Nonnewton. Fluid. Mech.* **2015**, *220*, 116–125. [CrossRef]
194. Aman, Z.M.; Olcott, K.; Pfeiffer, K.; Sloan, E.D.; Sum, A.K.; Koh, C.A. Surfactant adsorption and interfacial tension investigations on cyclopentane hydrate. *Langmuir* **2013**, *29*, 2676–2682. [CrossRef]
195. Corak, D.; Barth, T.; Høiland, S.; Skodvin, T.; Larsen, R.; Skjetne, T. Effect of subcooling and amount of hydrate former on formation of cyclopentane hydrates in brine. *Desalination* **2011**, *278*, 268–274. [CrossRef]
196. Lim, Y.A.; Babu, P.; Kumar, R.; Linga, P. Morphology of carbon dioxide–hydrogen–cyclopentane hydrates with or without sodium dodecyl sulfate. *Cryst. Growth. Des.* **2013**, *13*, 2047–2059. [CrossRef]
197. Lv, Y.N.; Wang, S.S.; Sun, C.Y.; Gong, J.; Chen, G.J. Desalination by forming hydrate from brine in cyclopentane dispersion system. *Desalination* **2017**, *413*, 217–222. [CrossRef]
198. Nakajima, M.; Ohmura, R.; Mori, Y.H. Clathrate hydrate formation from cyclo-pentane-in-water emulsions. *Ind. Eng. Chem. Res.* **2008**, *47*, 8933–8939. [CrossRef]
199. Sefidroodi, H.; Abrahamsen, E.; Kelland, M.A. Investigation into the strength and source of the memory effect for cyclopentane hydrate. *Chem. Eng. Sci.* **2013**, *87*, 133–140. [CrossRef]
200. Taylor, C.J.; Miller, K.T.; Koh, C.A.; Sloan, E.D., Jr. Macroscopic investigation of hydrate film growth at the hydrocarbon/water interface. *Chem. Eng. Sci.* **2007**, *62*, 6524–6533. [CrossRef]
201. Leea, J.; Kimb, K.S.; Seoa, Y. Thermodynamic, structural, and kinetic studies of cyclopentane + CO_2 hydrates: Applications for desalination and CO_2 capture. *Chem. Eng. J.* **2019**, *375*, 121974. [CrossRef]
202. Serikkali, A.; Van, H.N.; Pham, T.K.; Le, Q.D.; Douzet, J.; Herri, J.M.; Bouillot, B. Phase equilibrium and dissociation enthalpies of CO_2/cyclopentane hydrates in presence of salts for water treatment and CO_2 capture: New experimental data and modeling. *Fluid Phase Equilib.* **2022**, *556*, 113410. [CrossRef]
203. Ershov, E.D.; Lebedenko, Y.P.; Chuvilin, E.M.; Istomin, V.A.; Yakushev, V.S. *Problems of Hydrate Formation in the Cryolithozone. Geocryological Research*; MGU: Moscow, Russia, 1989.
204. Romanovsky, N.N. *Cryolithozone and the Zone of Hydrates of Natural Gases (the Problem of Relationship and Interaction). Problems of Geocryology*; MGU: Moscow, Russia, 1988.
205. Falenty, A.; Kuhs, W.F. Self-preservation of CO_2 gas hydrates-surface microstructure and ice perfection. *J. Phys. Chem. B* **2009**, *113*, 15975–15988. [CrossRef]
206. Kuhs, W.F.; Genov, G.; Staykova, D.K.; Hansen, T. Ice perfection and onset of anomalous preservation of gas hydrates. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4917–4920. [CrossRef]
207. Shimada, W.; Takeya, S.; Kamata, Y.; Uchida, T.; Nagao, J.; Ebinuma, T.; Narita, H. Texture change of ice on anomalously preserved methane clathrate hydrate. *J. Phys. Chem. B* **2005**, *109*, 5802–5807. [CrossRef]
208. Takeya, S.; Ripmeester, J.A. Anomalous preservation of CH_4 hydrate and its dependence on the morphology of ice. *Chem. Phys. Chem.* **2010**, *11*, 70–73. [CrossRef]
209. Gaidukova, O.; Misyura, S.; Morozov, V.; Strizhak, P. Gas Hydrates: Applications and Advantages. *Energies* **2023**, *16*, 2866. [CrossRef]
210. Circone, S.; Stern, L.A.; Kirby, H. The effect of elevated methane pressure on methane hydrate dissociation. *Am. Mineral.* **2004**, *89*, 1192–1201. [CrossRef]
211. Prasad, P.S.R.; Chari, V.D. Preservation of methane gas in the form of hydrates: Use of mixed hydrates. *J. Nat. Gas Sci. Eng.* **2015**, *25*, 10–14. [CrossRef]
212. Misyura, S.Y. Developing the environmentally friendly technologies of combustion of gas hydrates. Reducing harmful emissions during combustion. *Environ. Pollut.* **2020**, *265*, 114871. [CrossRef]
213. Misyura, S.Y.; Manakov, A.Y.; Morozov, V.S.; Nyashina, G.S.; Gaidukova, O.S.; Skiba, S.S.; Volkov, R.S.; Voytkov, I.S. The influence of key parameters on combustion of double gas hydrate. *J. Nat. Gas Sci. Eng.* **2020**, *80*, 103396. [CrossRef]
214. Misyura, S.Y. Dissociation of various gas hydrates (methane hydrate, double gas hydrates of methane-propane and methane-isopropanol) during combustion: Assessing the combustion efficiency. *Energy* **2020**, *206*, 118120. [CrossRef]
215. Misyura, S.Y. Dissociation and combustion of gas hydrates. *J. Engin. Thermophys.* **2022**, *31*, 573–579. [CrossRef]
216. Takeya, S.; Yoneyama, A.; Ueda, K.; Mimachi, H.; Takahashi, M.; Sano, K.; Hyodo, K.; Takeda, T.; Gotoh, Y. Anomalously preserved clathrate hydrate of natural gas in pellet form at 253 K. *J. Phys. Chem. C* **2012**, *116*, 13842–13848. [CrossRef]

217. Misyura, S.Y.; Donskoy, I.G. Dissociation of gas hydrate for a single particle and for a thick layer of particles: The effect of self-preservation on the dissociation kinetics of the gas hydrate layer. *Fuel* **2022**, *314*, 122759. [CrossRef]
218. Mimachi, H. Natural gas storage and transportation within gas hydrate of smaller particle: Size dependence of self-preservation phenomenon of natural gas hydrate. *Chem. Eng. Sci.* **2014**, *118*, 208–213. [CrossRef]
219. Misyura, S.Y.; Donskoy, I.G. Dissociation of a powder layer of methane gas hydrate in a wide range of temperatures and heat fluxes. *Powder Technol.* **2022**, *117017*, 10–14. [CrossRef]
220. Xu, J.; Bu, Z.; Li, H.; Wang, X.; Liu, S. Permeability models of hydrate-bearing sediments: A comprehensive review with focus on normalized permeability. *Energies* **2022**, *15*, 4524. [CrossRef]
221. Misyura, S.Y.; Donskoy, I.G. Improving the efficiency of storage of natural and artificial methane hydrates. *J. Nat. Gas Sci. Eng.* **2022**, *97*, 104324. [CrossRef]
222. Zhang, X.; Li, Y.; Zhang, S.; Yang, H.; Li, J.; Wu, Q. Experimental study on the effect of decomposition induction on the replacement process of CO_2–CH_4 hydrate in hydrate-bearing sediments below the freezing point. *Fluid Phase Equilib.* **2022**, *562*, 113562. [CrossRef]
223. Misyura, S.Y.; Donskoy, I.G. Ways to improve the efficiency of carbon dioxide utilization and gas hydrate storage at low temperatures. *J. CO_2 Util.* **2019**, *34*, 313–324. [CrossRef]
224. Gaidukova, O.; Misyura, S.; Strizhak, P. Key areas of gas hydrates study: Review. *Energies* **2022**, *15*, 1799. [CrossRef]
225. Misyura, S.Y.; Donskoy, I.G. Dissociation kinetics of methane hydrate and CO_2 hydrate for different granular composition. *Fuel* **2020**, *262*, 116614. [CrossRef]
226. Gaidukova, O.; Misyura, S.; Donskoy, I.; Morozov, V.; Volkov, R. Pool fire suppression using CO_2 Hydrate. *Energies* **2022**, *15*, 9585. [CrossRef]