

## Review

# A Review of Gas Capture and Liquid Separation Technologies by CO<sub>2</sub> Gas Hydrate

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**Abstract:** Gas hydrates, being promising energy sources, also have good prospects for application in gas separation and capture technologies (e.g., CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> hydrate; gas sequestration; desalination; kinetics; greenhouse gases



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## 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<sub>2</sub>S), carbon dioxide (CO<sub>2</sub>), 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  $1.8 \times 10^{16} \text{ m}^3$  and  $2 \times 10^{16} \text{ m}^3$  [8]. The highest estimates of natural reserves ( $3 \times 10^{18} \text{ m}^3$ ) 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  $1 \times 10^{15}$ – $5 \times 10^{15} \text{ m}^3$  [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  $1.1^\circ\text{C}$  to  $6.4^\circ\text{C}$ . The most likely warming prognosticates an increase in temperature by  $4^\circ\text{C}$ . 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  $12^\circ\text{C}$  [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  $0.5^\circ\text{C}$  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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>4</sub>–CO<sub>2</sub> 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<sub>2</sub>

The largest number of studies on CH<sub>4</sub>–CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>4</sub>/CO<sub>2</sub> replacement for CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> replacement: the phase state of the carbon dioxide used for injection; thermodynamic conditions during the synthesis of CO<sub>2</sub>-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<sub>2</sub> 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<sub>2</sub> storage is considered in [70]. After a long-term reformation, the methane recovery ratio increased from 24% to 85%. In addition, the CO<sub>2</sub> storage ratio was raised to 79–80%. The study of the micro-scale characterization of the sI hydrates containing a mixture of CH<sub>4</sub> and CO<sub>2</sub> was performed in [71]. A comparison of the technical and economic indicators of CO<sub>2</sub> 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<sub>2</sub> and N<sub>2</sub> 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<sub>4</sub> storage and CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> liquefaction [79]. The injection of CO<sub>2</sub>/H<sub>2</sub> gas mixture allows a high efficiency of natural gas hydrate exploitation and carbon sequestration to be achieved [80]. In CO<sub>2</sub>/H<sub>2</sub> 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<sub>4</sub>–CO<sub>2</sub>/H<sub>2</sub> is described in [82]. The efficiency of gas extraction

and the use of the promoter depend on the type of gas mixtures: flue gas ( $\text{CO}_2/\text{N}_2/\text{O}_2$ ); sulphur hexafluoride ( $\text{SF}_6$ ); and gas mixture ( $\text{SF}_6/\text{N}_2$ ) [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 ( $\text{CO}_2/\text{CH}_4/\text{H}_2\text{S}/\text{N}_2$ ) 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  $\text{CO}_2$  replacement of  $\text{CH}_4$  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  $\text{CO}_2$  is considered in [99].

The warm brine injection during  $\text{CH}_4/\text{CO}_2$  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  $\text{CO}_2$  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 (THF) was chosen as one of the first promoters [101]. In this paper, the regularities of the  $\text{CO}_2$  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  $\text{CO}_2$  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<sub>2</sub> 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]<br>Tetrahydropyran (THP) [126–128]<br>Cyclopentane (CP) [127,129–131]<br>Cyclobutanone [128]<br>Cyclohexane (CH) [128]<br>1,3 Dioxolane [132]<br>1,3,5 Trioxane [133]<br>Tetra-n-butylphosphonium acetate (TBP-Ace) [127]<br>Tetra-n-butyl ammonium bromide (TBAB) [102–106]<br>Tetra-n-butyl ammonium nitrate (TBANO3) [134]<br>Tetra-n-butylphosphonium bromide (TBPB) [135]<br>Tetra-n-butyl phosphonium chloride (TBPC) [135] |
| kinetic           | Enhances the kinetics of hydrate formation without affecting the thermodynamics | Sodium dodecyl sulfate (SDS) [115,136]<br>Tween [137]<br>Dodecyltrimethylammonium chloride (DTACl) [137]<br>L-methionine [127,138]<br>L-norvaline [127,138]<br>L-norleucine [127,138]<br>L-glycine [127,138]<br>L-tryptophan [127,138]<br>Metal particles and metal oxides [138]<br>Nanotubes [138]<br>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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> and solve the issues of carbon dioxide storage (greenhouse gas utilization) [170–173]. The installation of the continuous production and granulation of CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> hydrate and accelerates the hydrate growth [187].

Water volume affects the CO<sub>2</sub> 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<sub>2</sub> hydrate in a porous medium is studied in [189]. CO<sub>2</sub> 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<sup>+</sup>, 100% K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> 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<sub>2</sub> 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<sub>2</sub> sII hydrates are completely filled with gas molecules, while the small cages are filled with CO<sub>2</sub> 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<sub>2</sub> with cyclopentane hydrate in an aqueous salt solution for CO<sub>2</sub> capture are given in [202].

### 3.4. Dissociation of CO<sub>2</sub> 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<sub>4</sub>–CO<sub>2</sub> 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<sub>2</sub> 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  $\mu\text{m}$ ), 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  $\approx 1$  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  $\text{CO}_2$ – $\text{CH}_4$  hydrate in hydrate-bearing sediments below the freezing point is presented in [222]. The kinetics of  $\text{CO}_2$  hydrate dissociation (activation energy and pre-exponential multiplier) at negative temperatures differs from dissociation at positive temperatures [223–225]. When using a  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  hydrate is used.
- (ii) The use of gas hydrates for the  $\text{CO}_2$  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<sub>2</sub> 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<sub>2</sub> hydrate and concomitant reduction of energy costs.
- (v) To increase the duration of CO<sub>2</sub> 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<sub>2</sub> 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.

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