



Dissociation of natural and artificial gas hydrate



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HIGHLIGHTS

- Storage and combustion methane hydrate is simulated.
- Natural methane hydrate from the bottom of Lake Baikal was investigated.
- There is much longer area of self-conservation for natural hydrate.
- Dissociation was modeled taking into account the granules size distribution, size and pore density.

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ABSTRACT

Dissociation kinetics of natural and artificial methane hydrate were studied experimentally and theoretically. The artificial methane hydrate was produced in the reactor, and the natural clathrate was extracted from the bottom of Lake Baikal. The behavior of the natural gas hydrate decay is markedly different from the artificial one under non-isothermal conditions. For natural methane hydrates there is a much longer self-conservation area and a lower rate of dissociation caused by different initial defectiveness of samples. The proposed model takes into account the area of self-conservation and structural characteristics of the granules that allows qualitatively and quantitatively describing the dissociation. The non-isothermal dissociation was numerically simulated, taking into account heat and mass transfer, kinetics of phase transformation, gas filtering inside the granules and porous characteristics (size and density of pores). Different requirements are applied to technologies for efficient storage and combustion of gas hydrates. A more stable region of self-conservation of natural gas hydrate increases the efficiency of its storage and transportation. In this case, a durable crust of ice with a low concentration of pores is achieved for higher temperatures than for the artificially synthesized hydrate. In the course of dissociation of gas hydrate at negative temperatures of annealing, the density of the pores distribution in the formed ice crust decreases by eight orders that significantly changes the rate of decay during the dissociation. The simulation of dissociation of natural and artificial methane hydrates was implemented with a maximum density of pores and well agreed with the experimental data. Thus, it has been experimentally and theoretically shown that the density and size of pores dramatically affect the kinetics of dissociation. During storage, transportation and combustion of combustible gases solid hydrates it is necessary to determine the heat transfer coefficient and the temperature difference ΔT both for the outer medium (external boundary conditions) and the internal one (a layer of powder or pressed pellets). The dissociation rate of gas hydrates at negative temperatures $T < 0^\circ\text{C}$ is much more complex than for $T > 0^\circ\text{C}$ and currently there are no reliable calculation methods. The use of filtration model and structural parameters can effectively predict the behavior of gas hydrates at negative temperatures.

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1. Introduction

At present, studies of natural gas hydrates are devoted to both technical and fundamental issues and encompass a large number of related fields of physics. Further development of technologies using gas hydrates is also associated with the development of physical

models, describing the synthesis of particles into granules and pellets, and storage and transport of granules in huge tanks. It is expedient to define and explore the key factors affecting the stability of self-conservation. Self-conservation is storage of granules in the conditions when the gas hydrate has an abnormally low decay rate, allowing storing it for a very long time. To date, simulation of the synthesis and decomposition of gas hydrates is developed more carefully for positive temperatures. At the same time the dissociation at negative temperatures has not been fully explored, and there are many questions on the structure of gas hydrate, its strength, and

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resistance to decomposition during annealing. The question of considering structural characteristics in simulation remains open as well.

There are three main structures of gas hydrates: (sI), (sII) cubic structure and (sH) hexagonal structure (Sloan and Koh, 2008). Most natural gas hydrates have cubic structure. Gas hydrate deposits contain huge reserves of natural gas, and their intensive development will be started in the nearest decades. Prospects and challenges of natural gas hydrates as an energy resource are discussed in (Chong et al., 2016; Koh et al., 2009; Moridis et al., 2009). The feasibility of natural gas production from marine hydrate deposits considered in (Lu, 2015; Klauda and Sandler, 2005; Gornitz and Fung, 1994; Mekala et al., 2014). The gas hydrate technologies not only cover the global issues of energy resources and ecology of our planet, but the new energy sources such as gas hydrate batteries are being intensively developed (Obara et al., 2015). The efficient use of gas hydrates for biogas mixtures is presented in (Castellani et al., 2014). Engineering investigation of hydrogen storage in the form of clathrate hydrates and prospects of creation of hydrate production plants were presented in (Veluswamy et al., 2014; Nakayama et al., 2010). The maximum amount of H₂ stored in THF-H₂ hydrates (Hashimoto et al., 2007; Anderson et al., 2007) and double clathrates with tert-Butylamine considered in (Prasad et al., 2009). A comparison of energy efficiency for the three methods: single well depressurization, five-spot thermal stimulation method, the combination two methods was performed in (Wang et al., 2013). The steam assisted gravity drainage and the steam assisted anti-gravity drainage methods with thermal stimulation, depressurization, brine injection were considered in (G. Li et al., 2013; X.-C. Li et al., 2013; Wang et al., 2013). High-energy system with an engine generator using pressure working fluid composed of CO₂ hydrate is considered in (Obara et al., 2011). Recovery of methane from hydrate reservoir with gaseous carbon dioxide is presented in (Yuan et al., 2012). An application of carbon dioxide in a fixed bed reactor using the clathrate hydrate process was considered in (Babu et al., 2013). Methane production by depressurization with warm water stimulation in dual horizontal wells is considered in (Feng et al., 2015) and application of inverted five-spot water flooding method in cubic hydrate simulator is presented in (Li et al., 2014). In parallel with development of technologies for extraction of natural gas hydrate, theoretical and practical research on the synthesis and dissociation of artificial methane hydrates are being carried out intensively. Much attention is paid to the problems, related to transportation and storage of raw materials in large containers (Xie et al., 2010), and security issues (Takahashi et al., 2008; Gudmundsson and Borrehaug, 1996; Javanmardi et al., 2005; Kim and Kim, 2004; Mimachi et al., 2015; Rehder et al., 2012). Some estimates of risks for natural gas hydrate carriers were performed in (Kim et al., 2015; Kaehler and Hamann, 2012). Economic study on the transportation of natural gas hydrate (NGH) pellets were performed in (Rehder et al., 2012; Kanda, 2006). Features of gas hydrates transport in the form of pellets described in (Kaehler and Hamann, 2012; Rehder et al., 2012; Ota et al., 2002; Shirota et al., 2005; IMO. BLG14, 2010; Kim et al., 2010). The sintering process of spherical tetrahydrofuran (THF) hydrate particles and estimations of the sintering rate were investigated in (Uchida et al., 2010). The sintering rate of THF hydrate was controlled by the transportation of guest molecules through the vapor phase accompanied with water molecules.

The tankers carry liquefied natural gas at the temperatures below 110 K. Pelleted methane hydrate can be stored for a long time due to the phenomenon of self-preservation at the temperatures of 253 K. An increase in the temperature allows saving of about 40% of energy. The achieved economic benefit already today allows the use of new clean energy technologies. A lack of reliable physical ideas about natural gas hydrate dissociation does not allow us to move to

the higher temperatures and, thus, reduce significantly the storage cost. It is known that the lowest dissociation rate of methane hydrate is achieved at the temperatures of 265–267 K (Kuhs et al., 2004). Furthermore, the decay rate depends also on the grain size, powder layer thickness, morphology of ice grains, and ambient pressures. The structural characteristics of the surface envelope are investigated in (Kuhs et al., 2004; Nguyen et al., 2015; Falenty and Kuhs, 2009; Shimada et al., 2005). The effect of the thickness of gas hydrate layer and particle diameter on the decay rate was shown in (Falenty and Kuhs, 2009; Takeya et al., 2005; Mimachi et al., 2014). The effect of these key factors on the self-preservation mechanism and the metastable state was considered in (Kuhs et al., 2004; Falenty and Kuhs, 2009; Shimada et al., 2005; Takeya et al., 2005; Mimachi et al., 2014; Falenty et al., 2014; Misyura, 2013; Sato et al., 2013; Zhang and Rogers, 2008; Takeya and Ripmeester, 2010; Takeya et al., 2011, 2012; Stern et al., 2001, 2003; Lv et al., 2015; Prasad and Chari, 2015; Takeya et al., 2014). The supercooled water formation during gas hydrate dissociation is shown in (Melnikov et al., 2011, 2012; Madygulov et al., 2015). It is also important to note the different nature of diffusion at formation and decomposition of gas hydrates. The rate of gas hydrate formation and growth is limited by the medium thermal inertia and the gas diffusion rate in liquid and solid. The influence of environmental heat transfer on the mechanism of gas hydrate decay was considered in (Misyura, 2013; Cheng et al., 2015; Kaneko et al., 1997). It is shown that at a change in heat transfer, both the quantitative values of dissociation rate and qualitative nature of decay curves change. The number of dissociation minima for methane hydrate varies from zero to two, depending on the value of the external heat flux (Misyura, 2013). Combined effect of heat transfer and intrinsic kinetics on the decomposition of gas hydrate were considered in (Jamalludin et al., 1989; Khairkhan et al.; Masuda et al.). The rate of heat transfer and hydrate dissociation rate is proportional to power law functions of temperature difference (Kamath, 1983). The heat and mass transfer during the hydrate dissociation under thermal effect in porous media were considered in (Selim and Sloan, 1989). Heat conduction and convection included in model, when water and gas flows are considered (Durgut and Parlaktuna, 1996). The model of diffusive growth of gas hydrates was considered in (Vlasov, 2015). Decomposition of gas hydrate at positive temperatures occurs on the surface; it is determined only by the kinetics of phase transition and depends on the activation energy (Kim et al., 1987). Mathematical model of the natural gas hydrates dissociation with a moving Stefan boundary is considered in (Li et al., 2015). The porosity can be formed at both destruction and formation of gas hydrates. Kuhs et al. (Kuhs et al., 2000, 2004) first investigated the formation of meso- and macro-pores of gas hydrates using the scanning electron microscopy (FE-SEM). Clathrate hydrates were formed by the reaction of gas on ice Ih surface. Sublimation was studied for different types of gases. It was shown that the pore size depends on the type of the guest (gas molecules), embedded into the frame of the host (polar water molecules). For smaller gas molecules (CH₄, Ar, N₂), the pore diameter of 0.1–0.4 μm is substantially larger than that for the larger molecules of CO₂ (pore diameter of 0.02–0.1 μm) (Kuhs et al., 2000). The phenomenological kinetics model of the growth for the porous gas hydrate was proposed in (Salamatin and Kuhs, 2002). The porous structures were studied in a small growing hydrate layer at the liquid–liquid interface (Kobayashi et al., 2001). Natural gas hydrates, formed both from the continental and seafloor, are also indicate the presence of microporous structures (Suess et al., 2002). In (Staykova et al., 2003) the occurrence of porosity was associated with an excess of gas molecules at the time of gas hydrate formation. Porous gas hydrates themselves in nature are formed in the pore space of a hard rock (Dai et al., 2004; Dvorkin et al., 2003). Thus, we are faced with a variety of porosity: formation of meso- and macro-pores in a thin

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