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Effect of silica sand size and saturation on methane hydrate formation in the presence of SDS

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ABSTRACT

Abundant reserves of natural gas hydrates are hosted in the pores of sediment layers, and the hydrate-based technology could be widely used in industry. In this work, the formation kinetics of methane hydrate in a complex system containing silica sand and 300-ppm sodium dodecyl sulfate (SDS) solution were investigated at 275.15 K and 7 MPa. The hydrate was formed in different-saturated silica sand with particle sizes of 100, 150, 200, 300, and 400 mesh. The results indicated that in both the 50%- and 100%-saturated sand, a larger particle size exhibited a better methane storage capacity. In the complex system, the presence of SDS molecules significantly enhanced the hydrate formation process and weakened the effect of particle size on the hydrate formation rate. The difference in hydrate gas uptake formed in the differently saturated silica sand indicted that with an increase in saturation, the smaller-sized silica sands caused a more marked inhibitory effect. Finally, the different hydrate distributions in the 50%- and 100%-saturated silica sand revealed that a hydrate film formed quickly and preferentially on the surface of the silica sand, which was attributed to the adsorption of the SDS active groups and the presence of the silica sand surface. With the thickening of the hydrate film, the resulting volume expansion and stronger capillary force led to the migration of the liquid phase, which resulted in the hydrate distributions observed in the differently saturated silica sands.

1. Introduction

Gas hydrates are non-stoichiometric crystalline clathrates composed of water molecules and small-sized gas molecules that are trapped in the cages formed by water molecules via hydrogen bonding at low temperatures and high pressures. Studies have shown that many types of gases, such as methane, ethane, carbon dioxide, and nitrogen, can form the hydrate (Belandria et al., 2011; Rad et al., 2015). Hydrates can be classified into three categories according to the microscopic arrangement of the water molecules and the size of the gas molecules in the crystal nucleus: structure I (sI), structure II (sII), and hexagonal structure (sH) (Carroll, 2009; Karamoddin and Varaminian, 2014; Khodaverdiloo et al., 2016). Extensive amounts of gas hydrates are stored in nature and are globally distributed in marine sediments (~97%) and the terrestrial permafrost (~3%) (Rajput and Thakur, 2011). The estimated potential gas hydrate reserve is $> 1.5 \times 10^{16}\,m^3$ and even a conservative estimation of its resources is more than twice that of the combined fossil fuels (Shihui et al., 2017; Koh et al., 2009). Their high calorific value and small combustion pollution have made gas hydrates one of the most valuable and environment-friendly fossil fuels of the 21st Century.

Hydrates have a good gas storage capacity, storing as much as 183 vol of gas at standard pressure and temperature (Koh et al., 2012). They are widely used in many industrial areas such as natural gas storage and transportation, carbon dioxide capture, desalination, and refrigeration (Mimachi et al., 2014; Zhang, 2016; Park et al., 2011; Zhang et al., 2018). Therefore, due to their great significance in the improvement of the world energy supplies and their extensive applications in industry, these hydrates have attracted wide interest. The United States (Anderson et al., 2011), China (Wang et al., 2015a), Japan (Miyakawa et al., 2014), and Russia (Soyan, 2013) have tried to exploit hydrates in nature and all have made significant progress. However, their slow formation rate and relatively low storage capacity are major drawbacks that have hindered hydrate application in industry. According to previous studies, the presence of porous media increases the gas storage capacity and exhibits a positive effect on the

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nucleation process, thereby contributing to the rapid formation of the hydrate (Yan et al., 2005; Zanjani et al., 2012a). Thus, several laboratory studies on the improvement of hydrate formation using porous media have been reported in recent years.

While hydrate formation requires a low temperature, the process is exothermic; thus, the heat transfer conditions in the reactor are of great importance (Oignet et al., 2017). The presence of porous media improves the heat transfer conditions by increasing the coefficient of thermal conductivity. Moreover, because of the increased interface area of the porous media, hydrate formation benefits from the quicker 2D nucleation over the slower 3D nucleation, (Tóth et al., 2010; Khlebnikov et al., 2017). Therefore, many researchers have employed various porous media, such as glass sand (Wang, 2009), silica sand (Linga et al., 2009; Zhong et al., 2013), porous glass (Fitzgerald et al., 2014), active carbon (Kadhum et al., 2013), and marine sediment (Chatterjee, 2012), to study the characteristics of hydrate formation in pores compared to those observed in bulk water. Linga et al. (2012) compared the hydrate formation process in silica sand and pure water. The results revealed that the hydrate formation rate in silica sand was much higher than that in aqueous solution. Moreover, a higher water-to-hydrate conversion was found in experiments using porous media. Dai et al. (Dai et al., 2014) reported that the presence of the particle surface shortened the induction time over that in bulk water, thereby promoting hydrate formation. In an investigation of methane hydrate formation in a silica-based porous medium, Zanjani et al. (2012b) claimed that the addition of a small amount of colloidal silica sand greatly increased the gas storage capacity, while the CH_4 purification factor was much higher than that of the hydrate formed in the absence of porous media. This suggested that the presence of porous media is highly essential to enhance the hydrate formation process. In addition, according to the literature, hydrate formation is easily affected by the interface specific area, pore volume, and pore size distribution, depending on the particle size of the porous medium (Kang and Lee, 2010; Kim et al., 2011). Therefore, the particle size is a key factor for hydrate formation in porous media.

Many types of different-sized silica sand, such as Foundry 110 sand (Best et al., 2013), Leighton Buzzard sand (Kneafsey et al., 2005; Choi et al., 2014), and South China Sea sand (Zhang et al., 2016), have been adopted as porous media for hydrate formation. In the study by Bagherzadeh et al. (2011), magnetic resonance imaging (MRI) was employed to reflect the gas hydrate formation in different-sized (particle size: ≤75, 88–177, 125–210, and 210–279 μm) silica sand. They observed that hydrate formation in the smaller-sized samples was faster, while the hydrate formation in the coarser sand was found to yield a more irregular rate. Liu et al. (2008) studied the influence of particle size on hydrate formation using Raman spectroscopy. They reported that the cage occupancies and hydration numbers of the hydrate formed in the pores were similar to those of the bulk hydrate. When studying the influence of the porous media composition on hydrate formation, the results revealed that the formation kinetics changed with the composition of the porous media, with hydrate formation being inhibited when clay was added to the silica sand bed (Kumar et al., 2015). Sun et al. (2014) studied the effect of the silica sand pore size on the hydrate equilibrium conditions and observed a drop in the hydrate equilibrium temperature in fine-grained silica sand (≤ 4–250 μm). On the other hand, the influence of pore size on the hydrate equilibrium was negligible for coarse-grained sand in the range of 63–2000 μm. Water saturation is another important factor and the water characteristics inside the sediment are of great importance to elucidate the hydrate formation and dissociation mechanisms (Delli and Grozic, 2014). Zhang et al. (Peng, 2010; Peng, Qingbai et al., 2010) investigated the characteristics of vertical water transfer both in saturated and non-saturated porous media. At 100% water saturation, the hydrate formed on the top and center of the coarse sand and only at the top of the fine sand. On the other hand, the water transfer was very different in the three different porous media when they were only half saturated. Water at the bottom of the coarse sand migrated upward to form the hydrate. However, the reverse was observed in fine sand, while no significant vertical water transfer was detected inside the loess bed. By employing X-ray CT scanning, Rees et al. (2010) studied hydrate formation in sediments with different initial water saturation values. The results indicated that at 10% and 60% saturation, hydrate formation was relatively uniform in the sediment; however, between 30% and 40% saturation, the hydrate was no longer evenly distributed across the sand. This indicated that both the particle size and saturation in the porous media were important factors affecting hydrate formation.

The mass transfer conditions at the gas-liquid interface also promote hydrate formation (Davies et al., 2010). Previous studies (Raman et al., 2016; Veluswamy et al., 2015; Hayama et al., 2016; Kumar et al., 2013) have shown that the addition of a surfactant in the liquid phase lowers the mass transfer resistance at the gas-liquid interface by reducing the surface tension. This is one of the most effective ways to improve mass transfer. Many types of surfactants can enhance hydrate crystal growth and improve the gas storage capacity of the formed hydrate. Moreover, sodium dodecyl sulfate (SDS) promotes hydrate formation (Kakati et al., 2016; Jiang et al, 2016). Because the hydrophobic active groups in the ionized SDS will accumulate around the surface of the silica sand to avoid any contact with water in the solution. This eventually leads to the formation of many surfactant micelles that can dissolve more methane molecules due to micelle solubilization (Moroi, 1990). When the hydrate nuclei are formed around the surface of the silica sand, there are adequate gas molecules nearby for hydrate formation to occur. Therefore, combined to the positive role of the silica sand surface during hydrate nucleation, the complex system could enhance the hydrate formation process and improve the quality of gas storage. Considering the improvement in the heat and mass transfer conditions of hydrate formation when porous media and surfactants are employed individually, many scholars have combined the two to study the enhancing effect of this complex system. The results revealed that compared to that of the individual system, the improvement in hydrate formation in the complex system was significantly increased. Zhou et al. (2016) examined the effects of graphite nanoparticles and SDS on the induction time. Compared to the pure water system, the complex system significantly shortened the induction time of hydrate formation, while the promoting effect of the mixture was better than that of a single additive. Mohammadi et al. (2014) carried out hydrate formation experiments using nanosilver particles, SDS solutions, and their complex system. The results revealed that the combination of the nanoparticles and SDS produced the best increase in hydrate gas storage capacity. Thus, compared to bulk water, the combination of nanosilver particles and SDS increased the gas consumption by 93.9%. It is therefore very important to establish the characteristics of hydrate formation in the complex system. However, to date, most studies that have adopted a complex system to improve hydrate formation have only focused on the changes in some parameters of the formed hydrate, such as induction time, gas storage capacity, and water-to-hydrate conversion. Thus, there is limited information on the hydrate formation behavior in the pores of the medium in the presence of a surfactant and the distributions of the formed hydrate in porous media of different saturations.

In this study, a silica sand and SDS solution complex system was prepared to study the characteristics of hydrate formation. The experiments were conducted in a silica sand bed with different particle sizes at 50% and 100% saturation. The effect of the particle size on hydrate formation in silica sand with the same saturation in the presence of an SDS solution was therefore discussed. Subsequently, the experimental results at 50% and 100% saturation were compared to investigate the influence of the filling degree on hydrate formation and distribution. Finally, by observing the process of hydrate formation on the reactor wall through a glass window, a mechanism for hydrate formation and distribution in the silica sand and SDS complex system