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Experimental study on the effect of pore size on carbon dioxide hydrate formation and storage in porous media

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ABSTRACT

Hydrate method is feasible for solidification and storage of CO_2 gas into stratum sediments. In order to study the storage process of carbon dioxide in the form of hydrate into seafloor sediments, the formation characteristics of carbon dioxide hydrate was investigated in porous media and the formation experiment of carbon dioxide hydrate has been conducted in quartz sand porous media in high-pressure vessel of 1.8 L with pore size of 26.7 nm, 14.2 nm and 13.8 nm, respectively. The results show that, pore size of porous media has an important influence on the formation characteristics of CO_2 hydrate. Compared with porous media of 14.2 nm and 26.7 nm, the average formation rate and gas storage capacity of carbon dioxide hydrate attained 0.01328 mol/h and 53.558 L/L respectively. The results also indicated that, the smaller the pore size is, the longer the induction time and the larger the average formation rate and gas storage capacity of hydrate in porous media with pore size between 13.8 nm and 26.7 nm. It provided a theoretical guidance for solidification and storage of CO_2 into seafloor sediments in the form of gas hydrate.

1. Introduction

Carbon dioxide, as a greenhouse gas, is the main factor resulted in global climate warming gradually, so the effect of gradually increasing concentration of carbon dioxide discharged into the atmosphere has been concerned worldwide. As revealed in the report made by Pachauri and Reisinger (2007), the global temperature might increase 2–5 °C by the end of this century if the emissions of CO_2 don't be decreased at once. Therefore, there is a pressing need to decrease and control emissions of CO_2 in the atmosphere. The conventional methods of separating and capturing CO_2 usually include physical adsorption, chemical adsorption, cryogenic fractionation and membrane process, etc. However, these conventional methods have some shortcomings, such as high cost, large energy consumption, low capacity and high corrosion, and so on (Duc et al., 2007). Thus, it is necessary to find a new effective technology for storage and solidification of CO_2 gas.

Hydrate technology is a feasible method for storage of CO_2 gas into stratum sediments. Gas hydrate usually forms at relatively high pressure and low temperature, which can accommodate different size gas molecules (Sloan and Koh, 2008). Several properties of gas hydrate have attracted more attention of scientists for their huge potential in such practical applications as refrigeration and air conditioning (Delahaye et al., 2011; Darbouret et al., 2005), energy storage or transportation (Gudmundsson et al., 1998; Belosludov et al., 2007), or capture and sequestration of greenhouse gases (Adeyemo et al., 2010; Seo et al., 2005). CO_2 hydrate, for itself, is composed of CO_2 and water molecules at certain pressure and temperature. If all the cavities are filled, each volume of CO_2 hydrate may approximately contain 175 volumes of CO_2 at standard conditions (Sloan and Koh, 2008). This would effectually accomplish the process of solidification and storage for CO_2 in the form of hydrate. It is considered to be a feasible method for sequestrating and capturing CO_2 into sediments seafloor in the form of hydrate (Bickle, 2009; Haszeldine, 2009; Holloway, 2005). Therefore, it is necessary to investigate the formation characteristics in porous media such as average formation rate, gas storage capacity and stability condition of hydrate in porous media and so on.

Researchers have conducted lots of experiments and many constructive results were obtained in labs through a series of

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investigations. Handa and Stupin (Handa and Stupin, 1992) experimentally testified that the disassociation pressure of CH_4 and C_3H_8 hydrates were higher in porous media with small pores than those in bulk. Uchida et al. (1993) observed an equilibrium shift in silica glass with pore radius of 100 Å, 300 Å, and 500 Å. Besides, many other researchers reported the equilibrium shift of hydrates in porous media with pore radius smaller than 600 Å (Tohidi et al., 2001; Seshadri et al., 2001; Turner et al., 2005). It was thought that capillary effects of porous media with smaller pores caused the equilibrium shift (Handa and Stupin, 1992; Clarke et al., 1999; Clennell et al., 1999). Jiang et al. (2010) studied the formation and dissociation process of methane hydrate in porous media. The result showed that the temperature evidently controlled the dissociation process of methane hydrate in loess and the higher the dissociating temperature, the faster the dissociating rates of hydrate. Uchida et al. (2002) experimentally studied the effects of different media on the formation process of methane hydrate, and indicated that the equilibrium conditions of hydrates within these media were mainly affected by the pore sizes (Uchida et al., 2004). And the surface textures and mineral components of these media had tremendous influence on hydrate formation, too. Kumar et al. (Kumar et al., 2015) conducted formation experiments of hydrate in clay and indicated that low water contents of clay would inhibit the formation process of hydrate. And the effect of clay particles on formation process of hydrate was highly variable due to the low gas permeability and the different water activity in clay pores which depends on the water content. Many studies have shown that porous media had an important influence on formation characteristics of hydrate.

Zatsepina et al. (Zatsepina and Pooladi-Darvish, 2011, 2012) studied the storage process of CO_2 as hydrate and disused the storage capacity in different conditions, and the results showed that porosity affected the formation process of hydrate. Ding et al. (2013) investigated methane storage process in porous media and found that increased operating pressure and smaller particle size enhance storage capacity. Prasad et al. (2012) found that induction time of hydrate obviously shortened in porous media. Chari et al. (2013) reported that methane storage capacity in silica suspensions is comparable to the DW, particularly with optimum silica to water ratio. Sun and Englezos (2014) experimentally studied the storage process of CO_2 hydrate in a partially water saturated porous medium. The results showed that higher pressure was conducive to gas storage capacity of hydrate. Furthermore, initial pressure, temperature, and pore size of porous media affected the storage process of gas in hydrate.

However, there are plenty of experimental studies on formation and dissociation of CO_2 hydrate in porous media, there have few focused on quantitative influence of pore size on storage process of CO_2 in porous media. In this report, the formation experiments of carbon dioxide hydrate were conducted to study the influence of porous media on formation process of CO_2 hydrate in high-pressure vessel of 1.8 L. And the effect of pore size on the formation characteristics such as induction time, average formation rate and gas storage capacity of CO_2 hydrate was discussed. Conducting of this experiment can be helpful not only for understanding the formation characteristics of CO_2 hydrate in porous media with different pore size, but also provide a theoretical guidance for solidification and storage of CO_2 into sediment seafloor in the form of gas hydrate.

2. Experiment

2.1. Experimental apparatus

The schematic of the experimental setup is shown in Fig. 1. The main part of apparatus is a high-pressure vessel made of 316 L stainless steel, which can withstand the pressure up to 20 MPa and its internal volume is 1.8 L with including a buffer tank. The internal volume of the buffer tank is 5 L. A constant temperature bath is achieved by a cycling cooler through alcohol and controls the temperature of reaction system. A gas cylinder is used to supply CO_2 and control the pressure of the vessel. A vacuum pump is used for vacuumizing the high-pressure vessel before charging carbon dioxide. The platinum resistance thermometer (Pt100) is inserted into the high-pressure vessel to measure temperature with an accuracy of ±0.05 K. The pressure in the vessel is measured by pressure transducer with an accuracy of ±0.5%. The data acquisition system includes a data taker and computer accomplished by Agilent 34970A. Inside the vessel, two temperature sensors are installed at different positions and are employed to measure the temperature of gaseous phase and sediment in high-pressure vessel during the experiment.

2.2. Materials

Carbon dioxide used in the experiment was furnished by the Lanzhou Lanheng Special Gas Co. Ltd. with purity of 99.99%. The quartz sand was furnished by Tianjin Yuanli Chemical Co. Ltd in the experiment. Nitrogen used in the experiment was furnished by Zhejiang Tricyclic Chemical Reagent Co. Ltd. with purity of 99.9%. The water was deionized distilled water prepared in the laboratory.

2.3. Experimental procedures

In the experiment, the high-pressure vessel was the key part of experimental setup, which contained a buffer tank with its internal volume of 5 L. Before experiment, the quartz sand porous media was distributed homogeneously in high-pressure vessel and the formation process of hydrate was closer to the condition of natural sediments. Then 1 L of clean quartz sands with pore size of 26.7 nm was added in the high-pressure vessel. Accordingly, 450 mL of deionized water was added into the quartz sands and mixed and dispersed immediately and adequately. In this case, quartz sands were partially saturated by water. After that, the high-pressure vessel was sealed and immersed in the constant temperature bath and tested its tightness at vacuum conditions and a certain pressure condition, respectively. If the pressure change of the high-pressure vessel was confined within a certain range, it was considered to be good air tightness. After tightness testing, the vessel was purged with experimental gas and repeated at least three times. Then CO_2 was injected into high-pressure vessel until initial pressure achieved 3.6 MPa and set the temperature of constant temperature bath at 298.15 K. When the temperature was stabilized at 298.15 K, set the temperature of the constant temperature bath to 273.65 K and started to cool the reaction system immediately. And observed and recorded the variations of temperature and pressure during the formation process of CO_2 hydrate over time. Until the temperature and pressure changes were very negligible in the high-pressure vessel, stopped to cooling the constant temperature bath and the experiment finished at the same time.

Using the same method, the formation process of CO_2 hydrate was conducted in the quartz sand porous media with pore size of 13.8 nm and 14.2 nm. In the experiment process, 1 L of clean porous media with pore size of 13.8 nm was added in the high-pressure vessel. After that, 420 mL deionized water was added into the quartz sands and distributed homogeneously. And other procedures were similar as the experiment process of porous media of 26.7 nm.