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Characterization of CO_2 hydrate formation by temperature vibration

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ABSTRACT

A method of temperature vibration was proposed to promote CO_2 hydrate formation based on the dual nature of CO_2 solubility in hydrate-forming regions. The effects on carbon dioxide hydrate formation were investigated in a small scale reactor. The results show that the hydrate formation with distilled water in a quiescent system can be improved effectively by temperature vibration, and the pressure drop is increased by 30%. The effect is especially evident with 0.3% sodium dodecyl sulfate (SDS) additive using temperature vibration method, and large amount of hydrates are formed. The rest gas pressure is very close to the phase equilibrium value at setting temperature. Moreover, the pressure drop of CO_2 gas in the reactor is about 2.6 times of that without temperature vibration. With appropriate operation time of temperature vibration, hydrate formation period can be greatly shortened.

1. Introduction

The effect of global warming due to increasing concentrations of CO_2 in the atmosphere has been concerned worldwide. It is predicted that without CO_2 emissions reduction, this primary greenhouse gas may induce global warming of 2–5 °C by the end of this century [1]. It is a pressing need for reduction and control of CO_2 emission. Although various conventional methods for removing CO_2 have been suggested, there are still some critical problems such as energy consumption and low efficiency to be solved. It is a potential way to capture and storage CO_2 by means of gas hydrate [2–5].

CO_2 hydrate is a clathrate compound that CO_2 molecule is included in a cage-like structure formed by the water molecules [6]. In a unit crystalline cell of CO_2 hydrate, the framework is formed by a linkage of 46 water molecules through hydrogen bond with two pentagonal–dodecahedral cavities (small) and six tetrakaidecahedral cavities (large). It can contain as much as 160 volumes of gas under standard temperature and pressure conditions for one volume of CO_2 hydrate. Other potential applications include separation of gas mixture, cool storage, seawater desalination and gas storage through hydrate formation [7–9].

The main obstacles for CO_2 separation and storage technique are increasing hydrates formation rate, improving storage capacity, and reducing hydrate induction time. The formation of gas hydrate is a complex process with heat and mass transfer in gas, liquid and solid. The efficient contacting of the gas with water plays a key role in the above applications because agglomeration of the hydrate crystals creates a barrier which limits the conversion. One method to overcome the gas/water contact limitation is to contact the gas phase with water dispersed in the pores of silica gel and have the hydrate formed within the pores [10,11]. Other arrangements such as bubbles dispersed in water or water droplets injected into a gas atmosphere have been proposed [12]. Hydrate formation can also be improved by hydrate promoter or mechanical agitation which need for power consumption due to stirring [13–16]. Thus, it is necessary to study further to explore an effective method and give insight into its effects on CO_2 hydrates formation.

In this work, an experimental study of carbon dioxide gas hydrate formation has been conducted in a high-pressure reactor. The effects of temperature vibration on carbon dioxide hydrate formation were investigated in a small scale reactor based on the dual nature of CO_2 solubility in hydrate-forming regions.

2. Experimental

2.1. Experimental apparatus

The schematic diagram of the apparatus is shown in Fig. 1. The established experimental set-up mainly consists of a high pressure test cell where the hydrates are produced. The cell is a stainless steel cylinder with inner available volume of 680 ml. It is designed to operate up to 20 MPa. The reactor is equipped with a stirrer driven by a permanent-magnetic motor with feasible adjustment (range of 0–1000 r/min). The hydrate reactor was immersed in a thermostatic water bath that contained a mixture of water and ethylene glycol to maintain a constant temperature. The platinum resistance thermometer was used to measure the temperature with an accuracy of ±0.01 °C. The pressure in the cell was continu-

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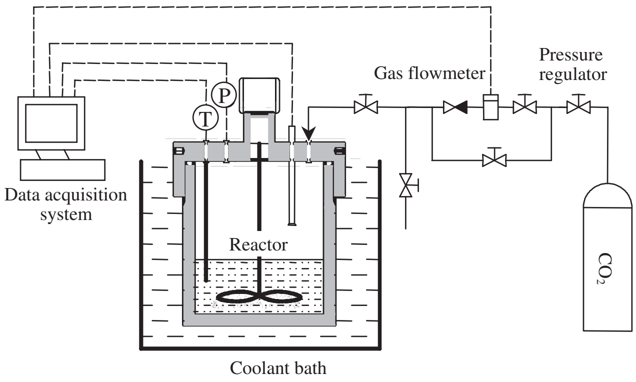

Fig. 1. Schematic diagram of experimental system.

ously measured by a 10 MPa digital pressure transducer with an accuracy of 0.3% of full scale. A mass gas flowmeter (model D07-11 M/ZM, Peking Jianzhong Instruments, Inc.) can be used to measure the amount of gas supplied to the cell during hydrate formation. The pressure and temperature are recorded by data acquisition system online.

2.2. Experimental description

Hydrate formation process mainly consists of three sequential steps: gas dissolution, nucleation and growth. Pressure and temperature are important for hydrate formation. Besides above factors, many others are also critical to the CO_2 hydrate formation, for example, the mass of CO_2 gas dissolved in the water.

Kojima et al. [17] pointed out that there are two different solubility in hydrate-forming regions, that is, the CO_2 solubility with hydrate decreases when the temperature goes down whereas it increases in the non-hydrate-forming region. Hashemi et al. [18] assembled a model to predict the gas solubility in water at equilibrium for carbon dioxide–water systems by applying the Trebble–Bishnoi equation of state along with the van der Waals and Platteeuw, and Holder models, as shown in Fig. 2. The model predictions were compared to available experimental data of Servio and Englezos [19] which showed a good agreement with each other. Based on the dual nature of CO_2 solubility in hydrate-forming region, a method of temperature vibration is proposed in the present study and it's effect on carbon dioxide hydrate formation was investigated in a small scale reactor.

The experiments are designed to operate at a constant volume system. A typical procedure involves cleaning and drying the inside of the cell and approximately 200 cm^3 of prepared water solution was charged into the cell for each experiment. The vessel was then closed and evacuated to remove residual gas in it with the vacuum pump. The hydrate-forming gas CO_2 was injected into the cell up to a pressure higher than the prescribed experimental value. The reactor was then kept at a steady temperature of 25 °C to ensure that the solution becomes saturated. After that, the pressure of the system was adjusted to a prescribed value. Put the reactor in the water bath that has been cooled at a setting temperature t_0 of about 0.5 °C (the equilibrium pressure is about 1.34 MPa at this value). The pressure was gradually decreased with the decrease of temperature at a certain time. Then hydrate formation started and it was tracked online through data acquisition system.

After a period of hydrate formation, raising the temperature of the cell to t_1 value to conduct the first temperature vibration process. The solubility of CO_2 was improved as the temperature increases. Keep the temperature at t_1 for some time, and then lower the temperature to initial value t_0 again. The increase of the subcooling degree results in fast production of CO_2 hydrate. Repeat this temperature vibration process several times as needed until the pressure in the cell remain steady, that means the hydrate formation is finished completely.

3. Results and discussions

3.1. Effect of temperature vibration on CO_2 hydrate formation with pure water system

Fig. 3 shows the effect of temperature vibration on CO_2 hydrate formation with pure water. Curve E1(P) and E1(T) show the pressure and temperature change respectively without temperature vibration, while E2(P) and E2(T) indicate the results with temperature vibration. It can be seen from E1(P) that CO_2 hydrate formed slowly with pure water in a quiescent system. The rest gas pressure remained at about 2.84 MPa after 1000 min. For curve E2(P), the pressure decreased slowly after 100 min reaction, and then temperature vibration was conducted the first time. Raising temperature to t_1 (4 °C), the pressure showed a little rise at the beginning. But after a while, it decreased slowly because of the increase of CO_2 solubility in water and hydrate formation is promoted. Decreased the temperature to initial value t_0 when the pressure change is not evident. Therefore, larger degree of subcooling resulted in rapid hydrate formation rate and drastic pressure

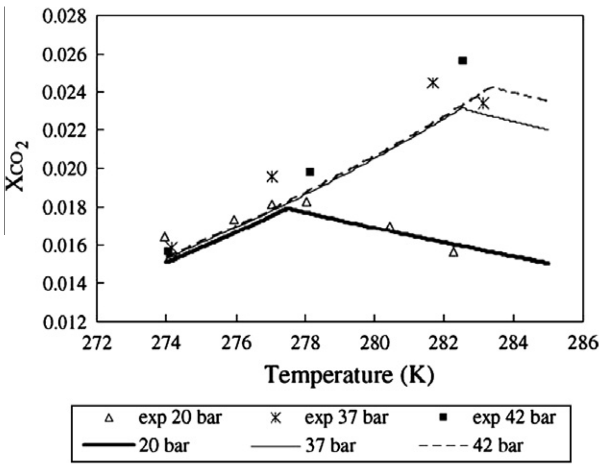

Fig. 2. Solubility of CO_2 in liquid water [18].

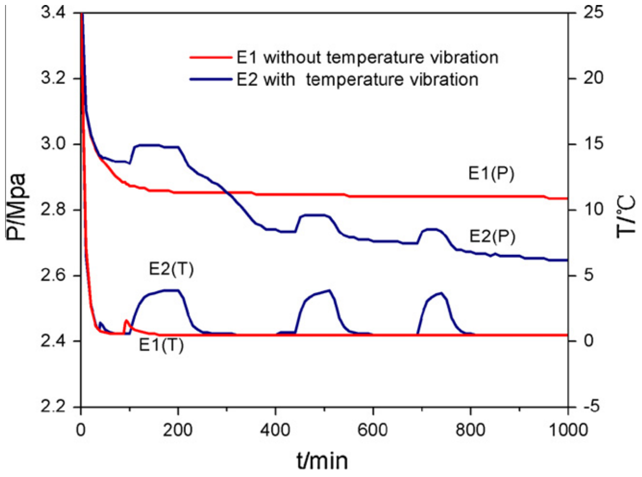

Fig. 3. Effect of temperature vibration on CO_2 hydrate formation with pure water.