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Micro-CT analysis of structural characteristics of natural gas hydrate in porous media during decomposition

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ABSTRACT

Natural gas hydrate in porous medium is a widespread form of hydrate in the natural world. In this study, porous media composed of sand at three particle sizes (0.85–1.18, 1.18–2.85, and 2.85–4.8 mm) were used to form natural gas hydrate by the Hydrate Synthetic Test System. The temperature and pressure during the formation process were described. The micro structural characteristics of the backbone, porosity, and the synthetic natural gas hydrate in porous media were studied by the High-precision Micro-CT Test System during decomposition. The results indicate that the hydrate is uniformly distributed and almost completely fill the pores of the porous media. The micro structural characteristics of the natural gas hydrate in porous media of three particle sizes and the backbones are also studied during the decomposition process. The relationship between the sand particle size and the maximum deformation of the backbone in the final stage of hydrate decomposition is determined.

1. Introduction

Natural gas hydrate is a snow-shaped or ice-shaped crystal. Substantial areas of pure gas hydrate are rarely found in the natural world. Geophysical exploration of hydrate layers and rock specimens indicated that massive gas hydrate deposits account for only 6% of its occurrence. The remaining gas hydrate deposits exist in porous media (e.g., marine sediments of the continental slope on shallow sea shelves or regions of permafrost) and cement of the surrounding media that generate a new pattern of energy storage: the hydrate reservoir. When the physical conditions of a hydrate reservoir changed with external interference, the hydrate could decomposes into gas and water and flows out through seepage channels. It is undisputed that natural gas hydrates are one of the largest sources of carbon on earth and a potential source of clean carbon based energy for humanity in the near future. Whilst there are no technology stoppers to exploit or produce methane from hydrates, specific technological breakthroughs will depend on the effective management of the sand and water during production, as well as the appropriate mitigation of environmental risks (Chong ZR et al., 2016).

Porous media are the carriers of gas hydrate in situ. Therefore, it is extremely important to investigate the formation and decomposition of hydrate in porous media using physical simulations. It is good to understand under which natural gas hydrate occur and the actual process of hydrate decomposition, and which are necessary if we are to create an effective, reasonable, and safe exploitation technology. Utilizing the sensitivity of X-ray computed tomography (CT) to examine the variations in the microstructure allows real images of hydrate in porous media to be obtained without disturbing the experimental samples. It can offer a new method of studying hydrate in porous media.

Research into hydrate in porous media is comparatively recently. In an early study, Makogon (1981) simulated the formation of hydrate in sandstones with different particle sizes. Handa and Stu, (1992) designed an experiment to determine the stabilization conditions for natural gas hydrate in porous media. Uchida et al. (1999) studied the stability of natural gas hydrate in porous glass with different pore sizes, and the variations in the stabilization pressure for natural gas hydrate formed in pores of different sizes. Aladko et al. (2004) investigated the decomposition temperatures and pressures of natural gas hydrate in mesoporous silica

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gels. Smith et al. (2002) constructed a phase diagram of natural gas hydrate in pores, based on experimental research, and determined the stabilization pressures and temperatures of methane hydrate in mesopores of various sizes. It is vital to understand the stability of natural gas hydrate in clastic deposits. Cha et al. (1988) found that natural gas hydrate remained stable at higher temperatures and lower pressures than in pure water when montmorillonite was present. Zhao et al. (2005) synthesized gas hydrate in porous media in a high-pressure reactor, and studied the formation and decomposition processes of these hydrate with multielectrode impedance measurements. Pu et al., (2005) used spiral CT to study the formation and decomposition principles for hydrate in frozen coarse sand, and the change process of hydrate in porous media will be represented by cross-section of CT images using the change of the average CT number in different areas. It showed that variations in the average CT numbers in various regions of specific sections of the CT image reflected the change processes of hydrate in porous media. Because spiral CT has low spatial resolution, only images with geometric proportions can be obtained. A relatively larger error will be generated when the CT number refers to the hydrate because of the CT number of water as a variable. With the CT number of water as a variable, moreover, the images generated with spiral CT only negligibly reflect the micro distribution and change processes of hydrate in porous structures. Natural gas hydrate in porous media has become a research hotspot in recent years, and their structural stability (Chari et al., 2014) and geochemical characteristics (Chen et al., 2009) has been investigated. Fauria and Rempel, 2011 examined the characteristics of gas intruding into water-saturated unconsolidated porous media. Alireza and Alireza, 2013 used capillary force to conduct a thermodynamic simulation of methane hydrate in porous media. Emily et al. (2011) studied the structures of hydrate in the Krishnae Sea area with the micro-CT scanning technique. Some chemicals such as tetrahydrofuran (THF) and cyclopentane (CP) are capable of reducing the hydrate phase equilibrium pressure and have been extensively investigated (Wang JQ et al., 2015) (Zhao JF et al., 2011), and (Seol and Myshakin, 2011), but the high volatility of these chemicals is undesirable for large-scale use. Jung and Santamarina, 2012 use optical, mechanical and electrical measurements to monitor hydrate formation and growth in small pores to better understand the hydrate pore habit in hydrate-bearing sediments. The growth processes of methane hydrates in porous media were investigated using attenuated total reflection infrared (ATR–IR) spectroscopic and optical microscopic techniques by Jin Y et al. (2012). The ATR–IR spectra revealed that hydrates in porous media grew in two steps. Two-step growth reflects the change in the nature of hydrates formed in porous media. Experiments at 8.0 MPa and 277.15 K were carried out in different porous media (Babu P et al., 2013), such as silica sand and activated carbon, to observe the formation and dissociation of methane hydrate in a specially designed crystallizer for mophology observation. The results show that pore space and its interconnectivity play an important role in methane hydrate formation in porous media consisting of silica sand or activated carbon.

In this study, the dynamic processes of hydrate formation and decomposition in porous media were investigated with a PW30-14 Natural Gas Hydrate Synthetic System (Fig. 1). The microscopic distribution of the hydrate, the evolution and displacement of the porous backbone during the decomposition process were studied using the μCT225kv FCB High-precision Micro-CT Test System (Taiyuan University of Technology).

2. Formation of natural gas hydrate in porous media

2.1. Formation processes of hydrate

Coarse sands were sieved four times by a different-sized mesh, and divided into three groups according to particle sizes (0.85–1.18, 1.18–2.85, and 2.85–4.8 mm), which were placed into individual cylinders and moderately compacted. The cylinders were made by metal mesh, with an outer diameter of 50 mm and a height of 150 mm. The cylinders were placed in the upper part of a natural gas hydrate reactor filled with methane gas; the lower part was filled with Sodium Dodecyl Sulfate solution at 300 ppm. At a preset pressure and temperature the natural gas hydrate began to form. This process was lasted until there was no longer pressure fluctuation. When compression pump did not work any more, this indicated that the hydrate had formed in porous medium.

The formation process lasted for about 4–5 h. An image of the formed hydrate was shown in Fig. 2. As seen in Fig. 2, the natural gas hydrate was formed in the pores of sands at the appropriate temperature and pressure. Outside and inside the pores were uniformly filled by hydrate. It was clear that the hydrate was uniformly covered onto the surfaces of the sand grains. Thus, sand grains acted as nuclei for the formation of the hydrate in porous medium. The crystals grew gradually until they filled the inside pore space. When the formed gas hydrate was ignited, a sustained flame blazed. The flame was smaller than that of generated by massive hydrate. During the reaction, the temperature of cooling bath was maintained at 274 K. When hydrate is formed, a large amount of reaction heat can cause the temperature fluctuation in the reactor.

2.2. Variations of temperature, pressure, and gas consumption during the formation of hydrate

As shown in Fig. 3, the hydrate in porous media was formed at 274–281 K and 5.9–6.0 MPa in reactor as temperature and pressure fluctuations. Under these conditions, the atomized water and methane gas combined, and formed hydrate in pore spaces. Gas consumption over time can be separated into three stages: initial stage, rapid formation stage, and completion stage in Fig. 3. During the reaction, the pressure was maintained at constant. Gas consumption is measured by the amount of liquid absorbed by the pressure pump 3 in Fig. 1.

The initial stage lasted for 100 min, and the rate of gas consumption was 1.5 L/min. The fluctuations in pressure and temperature were relatively small, and the gas consumption was minimal at this stage.

The rapid formation stage lasted for 80 min and the rate of gas consumption was 3.5 L/min. The temperature and pressure showed very frequent fluctuation in this stage, as large amounts of gas and SDS solution were formed into the hydrate.

The completion stage lasted for 100 min and the rate of gas consumption was approximately 0.01 L/min. When gas was no longer consumed, the hydrate were completely formed and the reaction stopped.

3. Microstructure of natural gas hydrate in porous media using micro-CT

3.1. Experimental method

3.1.1. Equipment

The μCT225kv FCB High-precision Micro-CT Test System, developed at Taiyuan University of Technology, was used. The specific parameters are as follows: the system imaging