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Effect of pressure vessel size on the formation of gas hydrates

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Abstract

A Seafloor Process Simulator (SPS) has been used for mesoscale experiments investigating the nature of hydrate nucleation and dissociation. The SPS is a 72 L vessel which establishes the pressures and temperatures required for methane and carbon dioxide hydrate stability. This paper describes the experiments that have been performed in the SPS and have been duplicated in the smaller Parr vessel (450 mL). It was found that experiments in the SPS resulted in hydrates consistently forming at lower overpressures and in shorter induction times than equivalent experiments in the Parr vessel. The variability of pressure and/or induction time for hydrate formation was not eliminated by using the SPS, but it appeared to be less dramatic (small coefficients of variation) when compared with a 450 mL Parr vessel. Based on the experiments performed using the SPS this reduction in overpressure and/or induction time required for the accumulation of hydrates may be attributed to increased bubble surface area, increased gas concentration, increased lifetime of bubbles, increased total volume of the SPS, or a combination of the above. Mesoscale experiments, such as those in the SPS, may perhaps be more representative of hydrate accumulation in the natural environment. Published by Elsevier B.V.

Keywords: Hydrates; Clathrates; Nucleation; Formation kinetics; Pressure vessel

1. Introduction

Gas clathrates or hydrates are ice-like solids formed when guest molecules are trapped inside cage-like structures of water molecules. Natural gas hydrates are stable at low temperatures (<10 °C) and high pressures (>3 MPa) typical of deep (>300 m) marine sediments or permafrost regions. Interests in natural gas hydrates include applications in gas storage (McTurk and Waller, 1964; Byk and Fomina, 1968; Davidson, 1973; Berner, 1992), desalination (Knox et al., 1961; Vlahakis et al., 1972; Barduhn et al., 1976), natural gas production (Collett, 1993), and well (Maini and Bishnoi, 1981) or seafloor stability issues in hydrate bearing sediments (Egrov et al., 1999; Haeckel et al., 2004). Methane is the most common gas component in natural gas hydrates that occur in permafrost (Collett, 1993) and deep marine sediments (Kvenvolden, 1993; Milkov and Sassen, 2000). Worldwide estimates of natural gas hydrates represent an approximate carbon content of 3000 Gtons along active and passive margins (Buffett and Archer, 2004). The abundance of natural gas hydrates is one reason that a variety of hydrate nucleation and dissociation investigations have been undertaken.

Hydrate nucleation and dissociation are studied in laboratories using high pressure vessels that are capable of maintaining the necessary temperature and pressure conditions required for hydrate stability. Many laboratory-scale pressure vessels have volumes ranging from 1 to 1000 mL for accurately investigating hydrate

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properties at small scales (Vysniauskas and Bishnoi, 1983; Parent and Bishnoi, 1996; Makogon, 1997; Morgan et al., 1999; Link et al., 2003). A variety of studies have also been conducted in the field (Brewer et al., 1997; Paull et al., 2003; Rehder et al., 2004; Tsouris et al., 2004) or at the field scale (1 or more wells) (Bybee, 2004; Chand and Minshull, 2004), examining hydrate properties in their natural setting. Intermediate between the typical small laboratory scale and in situ field scale would be mesoscale laboratory experiments utilizing large volume vessels capable of establishing natural gas hydrate temperature and pressure conditions.

The Seafloor Process Simulator (SPS) is a 72 L high pressure vessel (Phelps et al., 2001) ideal for mesoscale investigations of natural gas hydrates. The SPS is capable of maintaining pressure (up to 21 MPa) and temperature (−2 to 20 °C) conditions within the natural gas hydrate stability zone. Extensive research related to CH_4 (Riestenberg et al., 2003) and CO_2 hydrate (West et al., 2003; Riestenberg et al., 2004; Tsouris et al., 2004; Zatsepina et al., 2004) nucleation and dissociation has been conducted using the SPS.

The goal of this paper was to demonstrate the advantages of mesoscale examinations of hydrate nucleation under in situ temperature and pressure conditions. Though hydrate nucleation is a stochastic process (Bishnoi and Natarajan, 1996; Sloan, 1998; Zatsepina and Buffett, 2002) the SPS has proven to be a successful tool for reducing the impacts of stochastic behavior (smaller standard deviations and coefficients of variation for overpressure and induction time) when compared with smaller volume vessels. Mesoscale experiments in the SPS appear to more closely simulate in situ conditions for hydrate accumulation than experiments performed in vessels smaller than 1000 mL. This observation has been evident in various experiments that have been performed using both the SPS and a smaller (450 mL) Parr vessel. Previous experiments using the SPS and Parr vessel that investigated the effects of particulates (bentonite) and nucleators (Snomax and thawed water) have been reviewed and quantified. Hydrate formation in the vessels were compared by analyzing means, standard deviations, and coefficients of variation of overpressure and induction time for hydrate formation. Experiments examining the impact of different gas/water surface area sizes on the overpressure required for hydrate nucleation have also been described. We hypothesized that factors such as increased bubble surface area, increased gas concentration, increased lifetime of bubbles, and increased total volume may contribute in part or in combination to a greater likelihood of hydrate nucleation at lower overpressure or shorter induction times in the SPS. Accordingly, mesoscale gas hydrate research may prove useful in assessing seafloor hydrate stability issues and advance research for hydrate applications.

2. Facility and methods

Experiments were performed in both the 450 mL Parr vessel (Parr Instrument Company) and the SPS. The stainless steel Parr vessel (Fig. 1) has 2 quartz windows for visual observations, 6 access ports, a magnetically driven impeller, and a maximum working pressure of 21 MPa. Temperature was maintained by circulating chilled ethylene glycol through a thermal jacket surrounding the vessel (Fig. 1). The Parr vessel was designed for small-scale experiments, or as a means of testing experimental techniques prior to using the SPS.

The 72 L SPS high pressure vessel was constructed from corrosion resistant Hastelloy (Fig. 2). This vessel was designed to conduct mesoscale physical, geochemical, and microbiological research on gas hydrates. It weighs ~1400 kg and has a maximum working pressure of 21 MPa. Multiple sapphire windows with a diameter of 4.5 cm are available for visual observation or instrumentation. A total of 41 access ports are situated on the top and bottom lids and body of the vessel allowing for various types of instrumentation (i.e. temperature, pressure, pH,

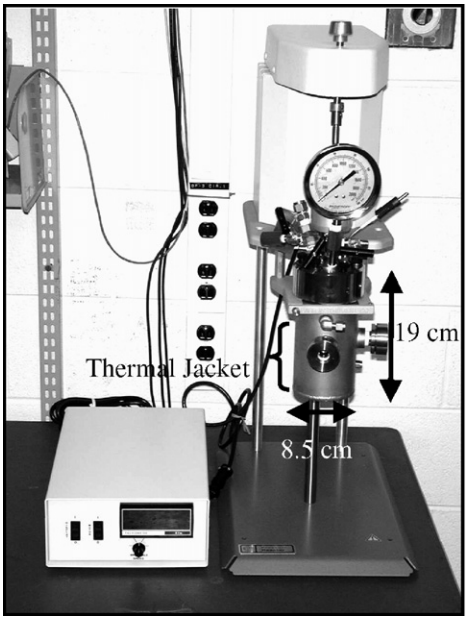

Fig. 1. The 450 mL Parr vessel with maximum working pressure of 21 MPa with two quartz windows. Shown to the left of the Parr vessel is the power supply for the magnetically driven impeller. Chilled ethylene glycol was used for temperature control and was circulated through a thermal jacket that surrounds the vessel.