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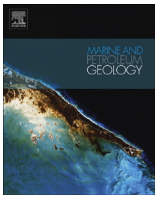

Laboratory study of methane hydrate formation kinetics and structural stability in sediments

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ABSTRACT

The natural gas hydrate deposits in the offshore of India are embedded in different sediments, namely clay rich silts and sands, coarse grain sand and volcanic fly ash. The variations in gas hydrate concentrations at different geological locations shows dependency on sediment mineralogy. It is also known that the particle size of the sediments plays an important role in hydrate formation and gas hydrate concentrations in sediments. We carried out systematic studies on the methane hydrate formation kinetics and methane hydrate volumetric yields, in stirred reactor experiments, using suspensions of synthetic silica and natural sediment from Krishna–Godavari (KG) Basin. The hydrate formation behavior in silica and KG basin sediment is also compared with the formation of methane hydrates in a "pure system" without sediment or added silica grains. Our results show that the hydrate formation kinetics is faster in 50 μm silica system followed by that in natural marine sediment. Observed methane hydrate yield in the laboratory is higher (~39%) in both the pure (no sediment) and 1 μm silica suspensions. The gas intake is much quicker (~375 min) in the suspension of 50 μm silica system, while the hydrate yield is noticeably less (~29.38%). The methane hydrates are characterized by Raman spectroscopy and they show characteristic structure I (sI) methane hydrate signatures, with a hydration number in the range 5.93–6.12.

1. Introduction

Gas hydrates (GH) are ice-like crystalline compounds, comprising of water cages forming through hydrogen bonding, and these cages are occupied by the suitably sized gas molecules. The encaged gas molecules are often referred as guest molecules, and usual guest molecules in natural gas hydrates are methane (CH_4), ethane, propane or carbon dioxide (Englezos, 1993). Much weaker Van der Waals interactions between the guest molecules and the surrounding water cage provide structural stability. Despite the fact that the gas hydrates look like ice, their physical properties are quite different; they can exist at temperatures well above the ice melting point at moderate pressures (Sloan and Koh, 2008). The four essential conditions for GH formation are (*i*) availability of host water molecules, (*ii*) suitable guest molecules with molecular diameter matching with available space within the host cages, (*iii*) moderately high pressure and (*iv*) lower temperature typically in the vicinity of freezing point of ice. Methane (CH_4) is the most common and predominant guest molecule (95–99%) in natural gas hydrates (NGH), and therefore we investigate the behavior of methane hydrates (MH) using silica/clay suspensions in this study.

The stability of submarine gas hydrates is largely dictated by the pressure and the temperature, gas composition and pore water salinity etc. However, the physical properties and surface chemistry of marine sediments may also affect the thermodynamic state, growth kinetics, spatial distributions of gas hydrates (Clennell et al., 1999). Gas hydrates have been inferred to exists in the Saurashtra and Kerala–Konkan Basins along the east coast of India. Seismic evidence for the presence of gas hydrate also exists in the Krishna–Godavari (KG), Mahanadi and Andaman sea regions of eastern India (Sain and Gupta, 2012). The NGHP-Expedition 01 (JODIES Resolution) confirmed the presence of hydrates in the KG Basin, Mahanadi Basin and Andaman region (Collett et al., 2008). The sedimentary property at these locations reveals that they are different from each other, e.g., clay rich marine sediment in KG Basin, coarse clay-rich silts and sands in Mahanadi and volcanic fly ash in Andaman (Sain and Gupta, 2012). Ginsburg et al., 2000

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demonstrated the role of sediment grain size on controlling the presence of hydrate at various sites on the Blake Ridge. Experimental results of Kawasaki et al. (2009) on sediments from the eastern Nankai Trough, indicate that particle size and clay contents are the two key factors determining the saturation level of gas hydrate in sediments; the finer the particle size and/or the higher the clay content, the lower the hydrate saturation. Therefore it is necessary to investigate the hydrate formation mechanism using host sediments to understand the role of mineralogy and grain size effects on the formation and structural stability of gas hydrate deposits.

In the geological environment the hydrate formation can occur very quickly or may take a long time and previous laboratory reports show that the time required in converting the pore water to hydrate, using methane gas saturated water at about 17.4 MPa, was around 50 days (Spangenberg et al., 2005). However, in a stirred reactor system, gas hydrate form much faster and can be used to critically examine controls on gas hydrate formation. In a stirred system the water and gas interfacial area changes regularly, therefore, improves mass and heat transfer to increase the methane hydrate formation process (Hao et al., 2007). It is also well documented in the literature that the nucleation and growth of hydrates is considerably faster in stirred reactors (Hao et al., 2007; Ke and Svartaas, 2011; Prasad et al., 2012). Effect of the stirring speed on the kinetics of methane hydrate formation was investigated earlier and there is no simple correlation between stirring rate and nucleation rate (Hao et al., 2007). The higher stirring speed causes a reduction in hydrate induction time and an increase in hydrate growth rate (Hao et al., 2007). But beyond some critical speed (typically 1000 rpm for a laboratory reactor) the hydrate yield may decrease because of increase in the fluid temperature. On the other hand, at lower stirring speeds the hydrate induction time increases and the hydrate crystals formed tend to remain on the surface. Vysniauskas and Bishnoi (1983) have suggested an optimal stirring speed of 400 rpm or more to improve the efficiency of the process.

Mesoscopic tools including X-ray computed tomography (XTG) (Kneafsey et al., 2007) and Scanning Electron Microscopy (SEM) (Kuhs et al., 2006) are being used to investigate the morphology and spatial distribution of hydrate at the state of sediment pores. At molecular level, tools such as Raman (Uchida et al., 1999; Chari et al., 2014); Nuclear Magnetic Resonance (NMR) (Susilo et al., 2007) spectroscopy; X-ray and Neutron diffraction (Murshed and Kuhs, 2009) are used to analyze the molecular properties and structure of the hydrate phase. The features of micro-Raman spectroscopy can unambiguously provide information about the structure, the hydration number and the cage occupancy of encaged molecules in hydrate phase (Prasad et al., 2009; Sum et al., 1997; Chari et al., 2014). Additionally, chemical identification of the guest molecules is also possible using micro-Raman probe (Prasad et al., 2007). Further, we have used Raman spectroscopy to elucidate the structural information and hydration number of the methane hydrates synthesized within this study.

2. Experimental design

2.1. Materials and characterization

The silica particles of diameter 1 μm and 50 μm were synthesized using a modified Stöbers method (Nozawa et al., 2005; Sreenivasa Rao et al., 2005). The natural sediment was collected from KG Basin at a depth of ~40 m below sea floor (mbsf) in our previous cruise (Ramprasad, 2007) at latitude and longitude of 150.45.81N and 810.47.03E respectively. The silica/natural sediment with de-ionized ultra-pure water and a methane gas with a purity of 99.95% was used to synthesize the methane hydrates. In Figure 1, we show the morphology and elemental composition of the samples analyzed by a Field Emission Scanning Electron Microscopy (FESEM) and Energy-dispersive X-ray spectroscopy (EDX). SEM images show that the silica particles are mostly spherical in shape. However, the KG Basin sediment appears mostly as flakes. The bulk density of silica and KG basin sample is measured as 1.5 and 1.27 g cm^{-3}. Elemental analysis with an EDX system shows that the synthesized silica particles confirm the presence of Si and O_2 with a ratio of close to 1:2. Whereas in KG basin sediment the elemental composition consists of mainly SiO_2, K, Ca, Fe, MgAl etc., are corroborated with earlier report of KG basin mineralogy (Pattan, 2002).

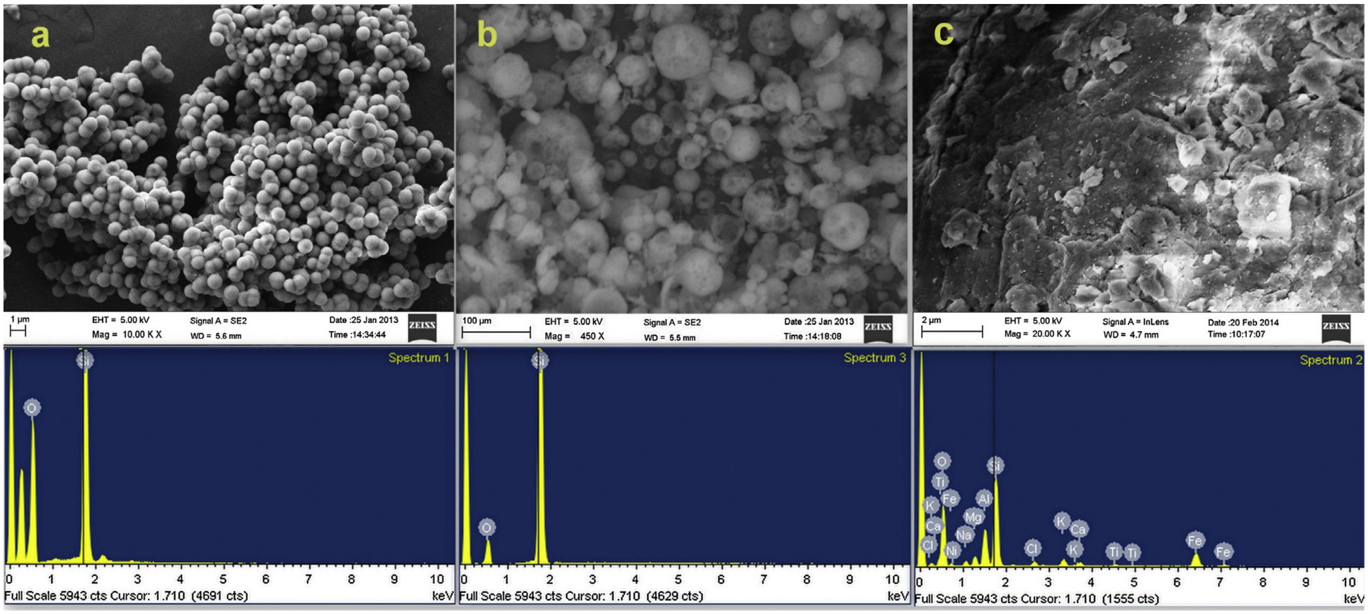

Figure 1. FESEM images and elemental compositions from EDAX spectrum of (a) 1 μm silica (b) 50 μm silica and (c) KG basin sediment used in the present study.