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Phase equilibrium of methane hydrate in silica sand containing chloride salt solution

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ABSTRACT

Hydrate equilibrium is the most important foundation for other hydrate issues, especially for marine environment condition. In this work, the silica sand containing NaCl/MgCl$_2$/CaCl$_2$ aqueous solution were used to simulate marine sediment for investigating methane hydrate equilibrium using isochoric multi-step heating dissociation method. All measurements were performed in a temperature and pressure range of (279.5 to 289.7) K and (8.32 to 17.52) MPa, respectively. The results suggest that the equilibrium of methane hydrate in fine-grained silica sand containing chloride salt solution shifts more greatly to the left relative to that in single silica sand or solution. This is because water molecules reduce more chances to combine with gas molecules that is caused by the capillary force and the electrostatic attractions from the surface and electrolyte ions. However, hydrate equilibrium in coarse-grained silica sand containing chloride salt solution is in rough agreement with that in ionic solution of the corresponding concentration that indicates that hydrate equilibrium is mainly influenced by ions while the impact of solid particles is negligible.

1. Introduction

Gas hydrates are non-stoichiometric crystalline solids that are composed of water molecules and gas molecules. Hydrogen-bonded water molecules form a lattice structure (cavity) and gas molecules are trapped in the cavity. Gas hydrates mainly occur in marine sediments, in which methane gas is a dominant component. Consequently, gas hydrates are regarded as one of the most promising new energy and have attracted much attention of all the countries in the world [1,2]. As well as a new energy, gas hydrates also have potential applications such as gas separation and transportation, carbon dioxide capture, desalination, cold storage, *etc.* [3–9]. During the process of gas production, gas hydrates will lose the original stability and then may result in a series of serious issues once they are out of control. At present, the exploitation techniques for gas hydrates involve hydrate dissociation to obtain free gas through heating, depressurization or inhibitor injection, *etc.* [10–13]. In order to ensure the safety, efficiency and economy of hydrate exploitation, the quantities of heating, depressurization and inhibitor must be precisely calculated and controlled. Otherwise, it is easy to result in a large number of free

gas suddenly released from hydrates causing an accident or geological disaster. For solving these problems, phase equilibrium of hydrates hosting sediment with ionic solution must be understood firstly. Owing to complex geological conditions of marine sediment bearing hydrates, phase equilibrium of hydrates are affected by multiple factors including seafloor temperature, pressure, sediment particle and pore water (seawater), *etc.* Usually, gas hydrates occur at the three-phase (hydrate + water + gas) equilibrium boundary where hydrates are very sensitive to the change of temperature and pressure. A small change of the ambient temperature or pressure may cause the dissociation of gas hydrates, which may trigger a submarine landslide or other environmental issues [14,15]. Therefore, it is very important to investigate the phase equilibrium of hydrates hosting natural sediment for the safe development and utilization of hydrate resources.

Marine gas hydrates occur in pores or cracks of sediment, so pore water (ions) and sediment particles may together affect the phase equilibrium of hydrates. Studies have shown that hydrate equilibrium temperature in the presence of ionic solution is depressed relative to that in pure water. These experimental data have been summarized by Sloan *et al.* [1]. In addition, the influences of various ions on phase equilibrium are different [16–18]. Marine gas hydrates usually lie below sulfate reduction zone and Cl$^-$ is the main anion. Lu *et al.* [17] found that although the anions

of SO_4^{2-} and Cl^- both affected phase equilibrium of methane hydrates in the presence of different pore water, the influence of Cl^- was more significant. Dickens et al. [19], Meakawa et al. [20], and Sun et al. [21] determined phase equilibrium of hydrates in the presence of different seawater samples and the changes of equilibrium temperature obtained by these authors were similar. In recent years, some results about phase equilibrium of hydrates hosting sediment have been also achieved. For example, Handa et al. [22], Seo et al. [23], Kang et al. [24], Zhang et al. [25,26] and Lee et al. [27] used porous silica gel to simulate sediment and found that hydrate equilibrium temperature was depressed under the same pressure relative to that in pure water. Uchida et al. [28] and Anderson et al. [29] employed porous glass for sediment sample and obtained the same conclusion. David et al. [30] and Englezos et al. [31] thought that the silica suspension and bentonite sample used in experiments had no obvious effect on methane hydrate phase equilibrium. But Cha et al. [32] and Ouar et al. [33] indicated the phase equilibrium temperature of natural gas hydrates was reduced by 2 K in 34 g · L^{-1} bentonite suspension. Uchida et al. [34] discovered that phase equilibrium of methane hydrates in silica sand and sandstone shifted to the lower temperature region while the dilute solution of bentonite had thermodynamic promoting effect on methane hydrate. Turner et al. [35] utilized Adriatic sandstone with an average pore radius of 55 nm to investigate phase equilibrium of methane hydrate and suggested that the equilibrium condition was not changed. Based on the experimental results, the theoretical pore radius that could affect hydrate equilibrium was calculated. Sun et al. [36,37] measured hydrate equilibrium in silica sand and the results indicated that hydrate equilibrium condition depended on the particle size. As discussed above, phase equilibrium of gas hydrates is obviously changed in the presence of ionic solution or seawater, namely hydrate formation will be inhibited. However, whether phase equilibrium of gas hydrate hosting sediment is changed or not depends on the properties and accumulation state of sediment. In general, hydrate phase equilibrium will not be changed in coarse-grained sediment, but it will be changed in fine-grained sediment. At present, the reports about phase equilibrium of hydrate hosting sediment containing ionic solution are rare. Yang et al. [38] determined that the phase equilibrium temperature of methane hydrate was depressed in the mixtures of artificial soda glass and NaCl aqueous solution, but they did not compare the contribution of ions and sediment. Lu et al. [39] investigated the phase equilibrium of methane hydrate in nannofossil-rich claystone column and the results showed that the phase equilibrium temperature of methane hydrate was reduced by (0.4 and 1.5) K relative to those in seawater and pure water, respectively. Sun et al. [21] found the equilibrium condition of methane hydrate in sediment sample from South China Sea was mainly affected by ions of seawater. Similarly, carbon dioxide hydrate equilibrium in the mixtures of coarsed-grained silica sand and NaCl solution was in agreement with that in NaCl solution with the corresponding concentrations [40].

Marine hydrates occur in sediment containing seawater (ions), so the equilibrium of hydrates in the complex system must be understood firstly in order to confirm hydrate formation mechanism, distribution and resource. Although the work on hydrate equilibrium condition is earlier and there are already some conclusions, many problems still need further research, especially for marine environment condition since it is the most important foundation for other issues. According to the literature [41], silica sand is one of main mineral compositions in sediment bearing hydrate and Cl^- is the major ion in seawater. Besides, marine gas hydrates usually occur below sulfate reduction zone where Cl^- is the main anion. Consequently, the mixtures of silica sand and $NaCl/MgCl_2/CaCl_2$ aqueous solution were used to simulate marine sediment bearing hydrate for investigating the equilibrium condition of methane hydrate and discussing the predominant influencing factors in this work.

2. Experiments

2.1. Experimental equipment and method

The experimental equipment consists of hydrate reactor, temperature control system, data acquisition system and gas supply system, as shown in figure 1. The effective volume of the reactor is 150 ml and it can withstand a maximum pressure of 40 MPa. The volume ratio of methane gas and silica sand in the reactor is 9:5. Free methane gas occupies the upper space. During loading the samples, silica sand and solution were alternately put into the reactor and then compacted with a rubber hammer. Meanwhile, enough time was also given for solution to fully saturate silica sand. During experiments, the temperature probe
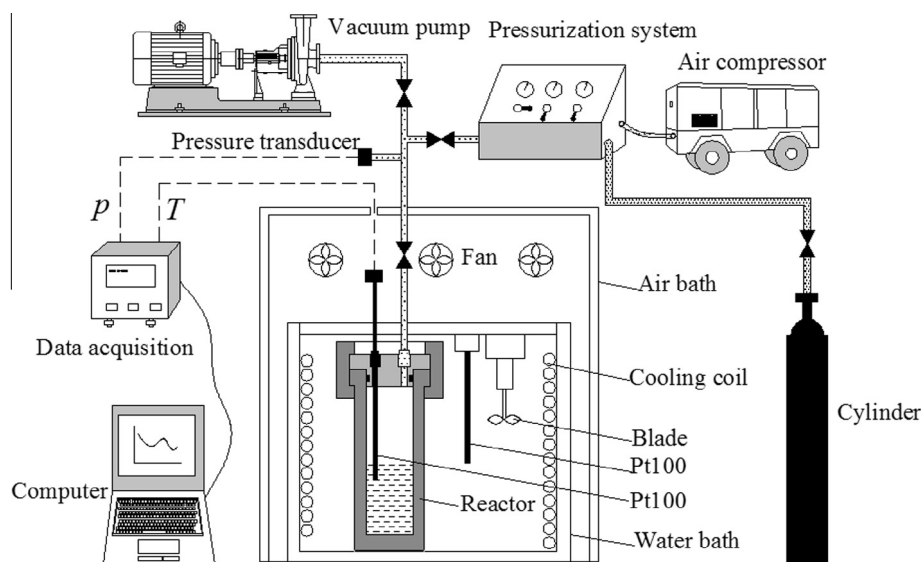

FIGURE 1. The experimental equipment for hydrate equilibrium.