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Particle size effect on the saturation of methane hydrate in sediments – Constrained from experimental results

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ABSTRACT

Except for those occurring at seafloor, most of natural gas hydrate form in sediments and are subject to the influence of sediment. Among these factors, the particle size effect on hydrate saturation level in sediment have been studied with a series of silica sands with various sizes, and the results obtained clearly indicate that particle size does play an important role in affecting the saturation level of hydrate in sediments. The proton relaxation times of water confined in the same series of silica sands, which were determined with NMR measurement, show logarithmic relationship with particle size. By comprehensive consideration of the results of hydrate saturation and water proton relaxation times, the particle size effect observed is tentatively explained by the water availability for hydrate formation in sediments.

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1. Introduction

Natural gas hydrate is a potential energy resource, because it occurs widely on continental slope and permafrost around the world and has been estimated hosting about twice the amount of organic carbon that is reserved in other conventional oil and gas resources. For the exploitation of natural gas hydrate, the exact estimation of gas hydrate reserve of a certain reservoir is indispensable, which largely depends on the information about hydrate distribution in sediment sequences and hydrate saturation in a specific sediment layer. Such information of a hydrate reservoir can be roughly obtained from regional geophysical investigations (Holbrook et al., 1996; Westbrook et al., 2008; etc.) and get refined by logging results (Collett, 2001) from a drilling well and direct geological and geochemical studies of the cored sediments (Matsumoto et al., 2004). It has been found that gas hydrate is preferentially enriched in certain types of sediments, for example in sands (Collett et al., 1988; Uchida et al., 2004; Uchida and Tsuji, 2004 etc.), in foraminifera rich sediments (Zhang et al., 2007), etc. However, difficulties have been met when pursuing quantitatively

understanding of gas hydrate distribution in sediments. For geophysical investigation, this is mainly arose from that interpretation of the regional or logging geophysical data relies on a certain model about the existence of gas hydrate in a sediment pore and generally yields results with large uncertainty (Ecker et al., 2000). It was expected that direct study of natural sample could provide reliable results, but the nature of gas hydrate, being stable only under relatively high pressure and low temperature, makes it difficult as well. Because sampling is a process that moves gas hydrate from its stable regime in the reservoir to unstable conditions on a drilling platform, natural gas hydrate samples rarely have been recovered intact. By these reasons, up to now the distribution and saturation level of gas hydrate in sediments can just be estimated very roughly.

Except for those occurring as outcrops on the seafloor, natural gas hydrates are found existing in sediments. No doubt, the sediment matrix will exert an influence on the formation and accumulation of gas hydrate. It has been reported that the stability condition of methane hydrate will shift to low temperature by 0.5 °C in nannofossil-rich sediments (Lu and Matsumoto, 2002), and it is also found that hydrate saturation in sediments is closely related to sediment particle size (Ginsburg et al., 2000; Uchida et al., 2004). However, natural sediments contain complex constituents, such as mineral particles, organic debris, pore water,

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fossil remains, etc., so it is difficult to specify the role of each component when studying natural sediments as a bulk.

To overcome the barriers mentioned above, it is better to elucidate the role of a specific factor in a system where this factor plays the main role. Among the various factors that may affect gas hydrate formation and accumulation in natural sediments, we select two of them for the current research: one is particle size of sediment, and another is water confined in sediment pores. The particle size of sediment is among one of the important factors that may affect gas hydrate formation in sediments, because it is the parameter to category sediments into different types, for example, gravel, sand, silt, etc. Gas hydrate forms from water and gas under certain condition, so we guess sediment may play its role in affecting hydrate formation through water. The water confined in sediment particles is kind of water in porous media, because it exists in the pore fabricated with sediment particles. There have been reports that the water confined in porous media has different physical and chemical properties from bulk water (Findenegg et al., 2008; Hills et al., 1996; Ricci et al., 2009). Kleinberg and his colleagues have done extensive studies of water in rocks with low-frequency NMR (Kleinberg et al., 1994, etc.), and they suggested that the properties of fluids in rocks were determined by the ratio of surface/volume. However few such researches have been performed with unconsolidated sediments, and none have been done to connect the water states with hydrate saturation in sediments. This research aimed at investigating the effect of the particle size on hydrate saturation in sediments through experimental study of hydrate saturation in silica sands with various sizes and tried to understand the mechanism by investigating the proton relaxation times of water confined in sands.

2. Experiment

As to the studies of the mineral compositions in the continental slope sediments through DSDP (Deep Sea Drilling Project), ODP (Ocean Drilling Program), IODP (Integral Ocean Drilling Program) and other marine geological surveys, the main mineral compositions of sediments are quartz, feldspar and clay minerals. As a result the experiments investigating particle size effect were carried out with silica powders. Although sII and sH gas hydrates have been identified in nature (Lu et al., 2007), the majority of the natural gas hydrate samples recovered up to now are sI methane hydrate, so the saturation of methane hydrate in various sediments has been investigated. Because natural marine sediment is saturated with aqueous solution with the salinity of ~3.5 wt%, predominantly composed of NaCl (Gieskes, 1975), the test specimens investigated in this research were saturated with 3.5 wt% NaCl solution. The silica sand was from Sigma–Aldrich with purity $\geq 99\%$, and the methane gas was $>99.95\%$ in purity from Praxair Canada.

To examine the particle size effect, a series of silica powders, ranging from coarse sand to medium silt (from 1000 μm to 20 μm), were tested for the conversion degree of water to hydrate and hydrate saturation.

Before the test specimen was charged into a polyethylene bottle, it was saturated with 3.5 wt% NaCl solution. To avoid the diffusion problem, the bottle was punctured a number of holes. After the test specimens were set in a pressure vessel, with the capacity to be used up to 15 MPa, the vessel was evacuated for about 10 min. Then, methane gas was charged into the vessel up to a pressure of 12 MPa, and the vessel was placed in a 3 °C incubator room. The reaction between pore water and methane gas was thought nearly complete, when the vessel pressure had not changed for about one week. As to our observations, generally it took about one month for the reaction to be complete. Upon sample recovery the pressure vessel was sat in a liquid nitrogen bath to avoid hydrate dissociation. The conversion

degree of water into hydrate and the hydrate saturation in a tested specimen was estimated from the amount of gas released from a known volume of this specimen. The determination of the amount of gas and the volume of hydrate followed the method described by Lu et al. (2005a,b, 2010). The error associated with this analysis is generally less than 3%.

For the formation of gas hydrate, one of the indispensable components is water. In sediments, gas hydrate forms from the water being confined in the pores of sediments. Thus, it is reasonable to conjecture whether the difference in hydrate saturation in different sediments is from the difference in water state. The state of water in confined space has been intensively studied through experimental and theoretical approaches (Rovere et al., 1998; Swenson et al., 2001; Gallo et al., 2002; Vyalikh et al., 2007; etc.). As to experimental and theoretical results, the water in a confined space has been thought to be in three states, bond, surface and bulk. The bond water contacts directly and interacts with the solid surface; surface water is next to the bond water and its structure is perturbed due to the presence of surface; bulk water locates from surface water to pore center and is with the same properties of bulk water. Experimental and theoretical studies have revealed that the bond and surface water extend about two molecular layers (Gallo et al., 2002). Hills et al. (1996) found that the proton relaxation rates can be used to characterize the states of water in a confined space. Kleinberg et al. (1994) reported that water relaxation in rocks depended on the surface-to-volume ratio. For exploring the possible relationship between hydrate saturation and water state in sediment, the water proton relaxation times were investigated in the same series of sediments that were used for hydrate saturation studies. The proton relaxation times, spin–lattice T_1 and spin–spin T_2 , of water confined in silica sands saturated with 3.5 wt% NaCl solution were performed at room temperature using an AVANCE 200 MHz Bruker NMR spectrometer. Although the relaxation is generally presented as relaxation rate, we reported the proton relaxation of water as relaxation time, following the tradition of NMR studies of natural materials such as rocks.

3. Results and discussions

The results about the conversion degree of water into hydrate and the saturation level of methane hydrate in the silica sands with various sizes are depicted in Figure 1. Obviously, the conversion degree of water into hydrate (Fig. 1A) and the saturation of methane hydrate (Fig. 1B) in the specimens studied are closely related to particle size. In the range from 20 to 200 μm , the conversion degree of water into hydrate increases dramatically with particle size increase, from 3% to 82%, corresponding to a pore saturation of hydrate from 4% to ~100%. It is noted that the conversion degree (~82%) of water into hydrate is almost constant when the particle size is over 200 μm (about the size of fine to medium sand), and the sediment pore is almost 100% occupied by hydrate at this saturation level.

Because the test specimens were all silica powder and only different in particle size, other possible factors affecting hydrate formation than particle size can be excluded. The results obtained clearly indicate that particle size plays a key role in determining hydrate saturation in sediments.

Figure 2 shows the relationship between the proton relaxation times (T_1 and T_2) with the particle size of silica sand. Both T_1 and T_2 show logarithmic relation with particle size: relaxation time becoming shorter with particle size decrease. This is consistent with the previous results that magnetization decays exponentially (Kleinberg et al., 1994). T_1 in silica sands range from 2.7 s to 127 ms and T_2 in silica sands change from 16.9 ms to 717 μs , when particle size decreases from 1000 μm to 20 μm . As the T_1 and T_2 of bulk

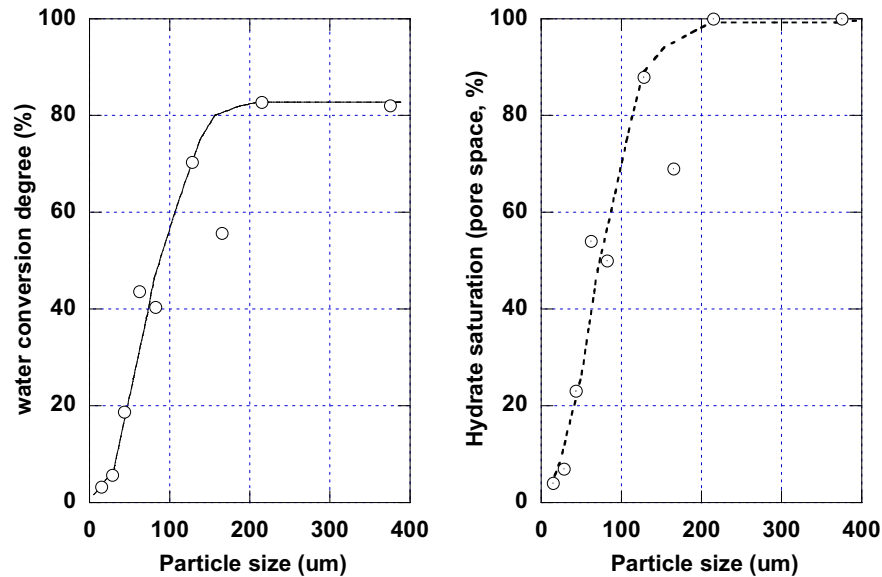


Fig. 1. The relationships between particle size and the degree of water conversion into hydrate as well as the hydrate saturation in silica sands.

3.5 wt% NaCl solution were determined as 3.0 s and 449 ms, respectively, the T_1 and T_2 of water proton confined in silica sands are all shorter than those of bulk solution, indicative of the confined effect of silica sands.

The relationships between the degree of water conversion into hydrate and the proton relaxation times (T_1 and T_2) are shown in Figure 3. It can be seen that the degree of water conversion into hydrate increases in a general linear mode with T_1 . The conversion degree also increases with T_2 increase in the range from 700 μ s to 6 ms but experiences almost no change after T_2 over 6 ms, which might be associated with the proportions of water states in pore, which will be discussed in detail in later section.

Because methane hydrate forms from and exists in contacting with pore water that is confined in silica sands and it has been suggested that hydrate formation is controlled by the water activity in electrolyte solution (Dickens and Quinby-Hunt, 1997), the particle size effect on hydrate saturation might arise from the

property of pore water. The material employed for this study is silica (SiO_2) sand, which has silanols at its surface. Silanols are functional and contain one or more $-\text{SiOH}$ groups. Neutron diffraction and theoretical analysis have found that water forms hydrogen bond with these silanol groups, and the influence of this interaction between water and silica surface can extend to pore center in case that water solution is confined in porous media (Thompson et al., 2007). The confined water has been found different from bulk water in several ways, such as less hydrogen bond numbers, less dynamics, etc., especially for the bond and surface waters, and this confined effect becomes stronger with the specific surface area increase in smaller pores (Takamuku et al., 1997). Hills et al. (1996) tried to estimate the activity of confined water with the relaxation time of water proton and found that the average water activity decreased with the decrease in particle size, or increase in surface-area/mass (specific surface area). They claimed that the interaction of water with silica surface only affect

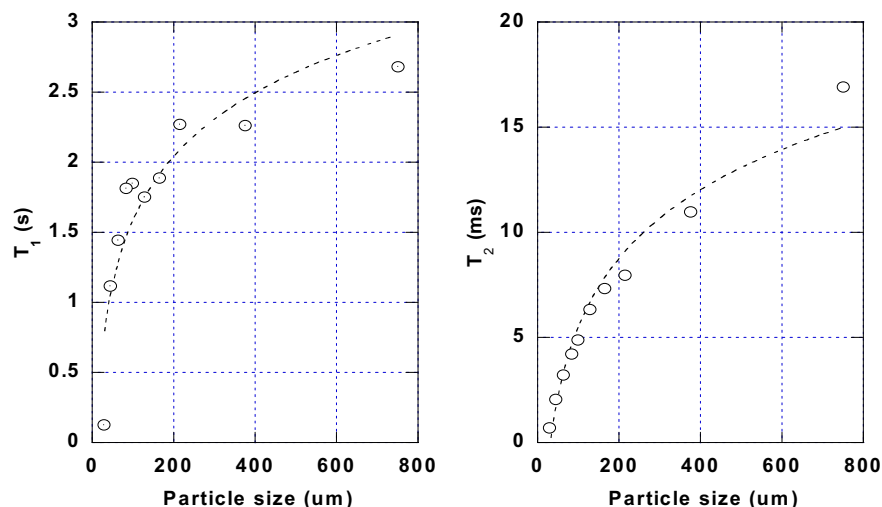


Fig. 2. The relationships between the particle size and the relaxation times (T_1 , T_2) of water in silica sands (the T_1 and T_2 of bulk 3.5 wt% NaCl solution are 3.0 s and 449 ms, respectively).

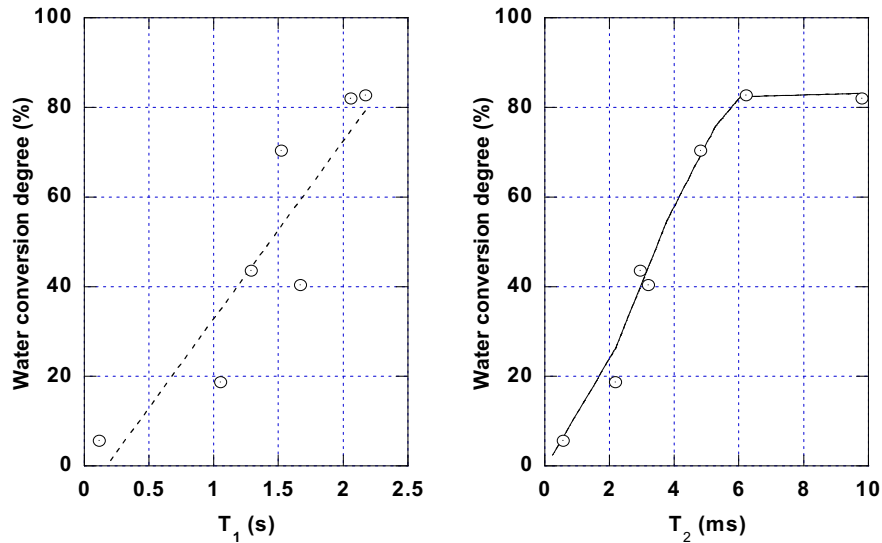


Fig. 3. The relationships between the degree of water conversion into hydrate and the relaxation times (T_1 , T_2) of water in silica sands.

the water near to silica surface, not more than two molecular layers from the surface, and the relaxation time measured by NMR represented the average of the reacted (bond and surface) water and the bulk water.

In our studies the silica sands in smaller particle size have with larger specific surface area, because the specific surface area is inversely related to particle size. As a result the water in silica sand with larger particle size will be subject to less influence of silica surface. Figure 4 shows the stability condition of methane hydrate in water saturated silica sands of 37–50 μm . It can be seen that the stability condition of methane hydrate is not significantly different from that in bulk water. Because the stability condition of hydrate is determined with the water surrounded it, this phenomenon might indicate that the hydrate is only formed in and surrounded with the bulk water in silica sands. However, as discussed previously, only about 6% of the water in the silica sands of 37–50 μm is converted into hydrate, much lower than the 82% in sands over the size of 200 μm . This implies that the proportion of the water available for hydrate formation might be different in silica sands with different particle size. As to the three-state model of water in confined space, in addition to bulk water there are bond and surface waters. Hills et al. (1996) proposed that the bound and surface water have

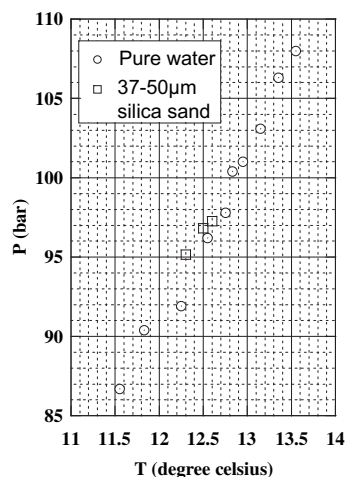


Fig. 4. The stability condition of methane hydrate in silica sands of 37–50 μm .

lower activity than bulk water. Comprehensively considering of these information, we consider that the bound and surface water is not available for hydrate formation and can be taken as unclathratable water. As the result, the particle size effect may be tentatively explained as that the proportion of bulk water in silica sands with smaller particle size is less than that in sand with larger size, because the specific surface area is larger and consequently more water will interact with the surface silanol groups. This is reflected in the shorter water proton relaxation times measured in smaller-size silica sands. As the relaxation time reported by NMR measurement represented an average of relaxation times of bound, surface and bulk water in silica sands, the higher the proportion of unclathratable (bound and surface) water will be in smaller silica sands as indicated by the shorter average relaxation time. Thus, the almost constant hydrate saturation after particle size over 200 μm might imply that the proportion of unclathratable water didn't have significant change after this particle size. Noticeably, different from the almost constant hydrate saturation after particle size over 200 μm , the relaxation time kept its trend of increase. This implies that particle size effect on hydrate saturation cannot be simply explained with the relaxation of water in silica sand, although certain relationship between them has been identified. This difficulty is largely due to the incomplete understanding of confined water. For example, Gallo et al. (2002) found that the bulk water in confined space is still different from the bulk water in open space, because the confined water has the same structure of bulk water at a higher temperature. As a result, further studies have to be conducted for a full understanding of this particle size effect in the future.

4. Conclusion

From the results stated above, the following conclusions have been obtained.

- 1) The particle size does play a significant role in affecting hydrate saturation,
- 2) The proton relaxation times (T_1 and T_2) show logarithmic relation with particle size: becoming shorter in silica sands with smaller size.
- 3) Fundamentally, with the consideration of the interaction of water with the silanol groups at the surface of silica sand the

particle size effect on hydrate saturation is tentatively explained arising from the less availability of water for hydrate formation in silica sands with smaller size.

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