

SEDIMENT CONTROL ON THE SATURATION LEVEL OF GAS HYDRATE IN NATURE ENVIRONMENTS

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ABSTRACT

A series of studies have been carried out to elucidate the sediment effect on the saturation level of methane hydrate in sediments. The specimens tested covered most of the natural sediment types, with various combinations of particle size and mineral composition. The results obtained 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. The observed particle size effect and clay effect on hydrate saturation can be accredited to the specific surface area of a sediment.

Keywords: gas hydrates, saturation, sediment, particle size, specific surface area

INTRODUCTION

Except for those occurring as outcrops on the seafloor, natural gas hydrates are found 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 boundary of methane hydrate will shift to low temperature by 0.5 °C in sediments [1], and it is also found that hydrate saturation in sediments is related to sediment particle size [2, 3]. However, sediment control on hydrate occurrence has only been described qualitatively, no quantitative information about how much hydrate can form in a specific sediment type is available, and the accumulation mechanism is not well understood.

The saturation level of gas hydrate in sediments is a key parameter for reserve estimation. Currently it is evaluated either from geophysical measurements or geochemical studies. The best way to learn about the occurrence of gas hydrate in nature is to study natural samples. However, due to the nature of gas hydrate, it being stable only at relatively low temperature and high pressure, natural gas hydrate samples rarely have been recovered intact because sampling is a process that moves gas hydrate from its stable regime in the reservoir to unstable conditions on a drilling platform. This makes it difficult to characterize gas hydrate in sediment directly using a natural sample. Moreover, natural sediments contain complex constituents, such as mineral particles, organic debris, pore water, etc, so it is difficult to

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specify the role of each component when studying natural sediments. As a result, it is better to elucidate the role of a specific factor in a system where that factor plays the main role. This research aims at understanding the effect of the particle size and mineral composition on hydrate saturation in sediments through a laboratory experimental approach.

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 compositions of sediments are quartz and clay minerals. As a result the experiments investigating particle size effect were carried out with silica powders. Among clay minerals, smectite and illite are the main components. Due to availability, kaolinite and montmorillonite were used as the representatives of the clay minerals to investigate effects of clay on hydrate saturation in sediments. As to our studies on the clay effect on the thermodynamic properties of gas hydrate, all of the clay minerals behave similarly except for montmorillonite, so to use kaolinite instead of illite will not cause significant differences. Although sII and sH gas hydrates have been identified in nature, 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. 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 medium sand to medium silt, were tested for the conversion rate of water to hydrate. To test the clay effect, a suite of sand (250-500 μm) and kaolinite mixtures were prepared at different ratios.

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 with an awl to give a number of holes around the bottle. After the test specimens were set in a pressure vessel, to be used up to 15 MPa, the vessel was evacuated for about 10 minutes. 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. When the pressure did not change in the vessel for one week,

this was taken as a signal that the hydrate formation reaction was complete, the pressure cell was immersed in a liquid nitrogen box to cool it down to avoid any dissociation upon sample recovery. The hydrate saturation in a prepared sample was estimated from the amount of gas released from a certain volume of hydrate. The determination of the amount of gas has been well described by Lu et al [4].

RESULTS AND DISCUSSIONS

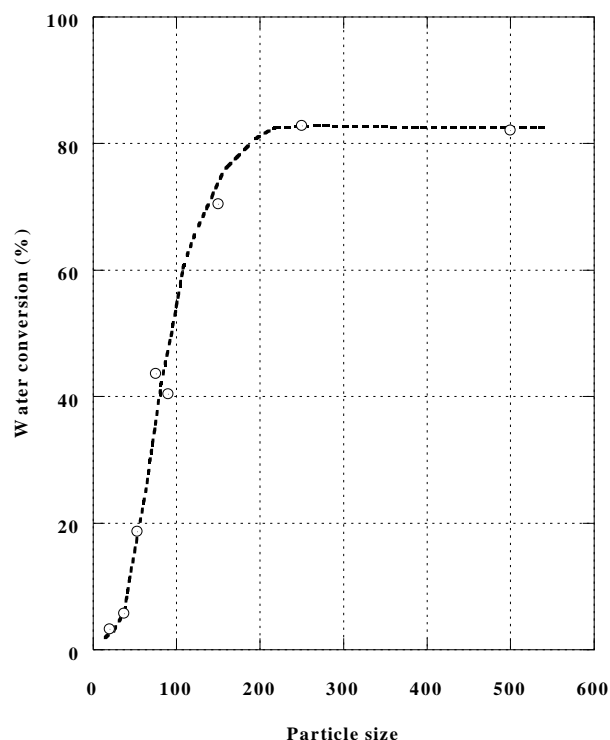


Figure 1. The relationship between particle size and the conversion rate of water into methane hydrate in silica powder.

The results obtained are depicted in Figure 1. Obviously, the saturation of methane hydrate in the specimens studied is closely related to particles size. In the range from 20 to 250 μm , the degree of conversion of water into hydrate increases dramatically with increase in particle size, from 3% to 82%, corresponding to a pore saturation from 4% to $\sim 100\%$. It is noted that the conversion level ($\sim 82\%$) of water into hydrate is almost constant when the particle size is over 250 μm . Because the test specimens were all silica powder and only different in particle size, the latter plays a

key role in determining hydrate saturation in sediments.

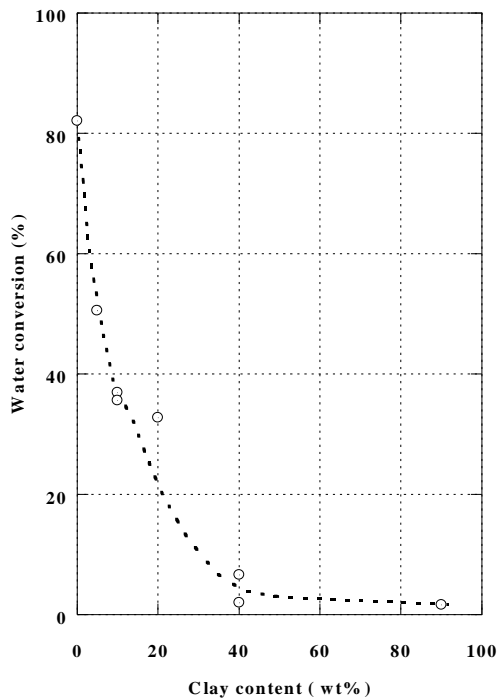


Figure 2. The relationship between clay content and the conversion level of water into hydrate in a sand-kaolinite mixture.

As shown in Figure 2, the water degree of conversion to hydrate in the sand-kaolinite mixture is well controlled by the clay content: decreasing dramatically with an increase in clay content. When the clay content is over 40%, the amount of pore water converted to hydrate is only about 2%, corresponding to a hydrate saturation lower than 3%.

Tohidi et al. [5] claimed that gas hydrate forms in the center of pores, and this has been supported by NMR observation on gas hydrates in sediments [6]. Because gas hydrates exist in the pore center in sediments, it will be surrounded by pore water, a kind of electrolyte solution (predominantly composed of NaCl) with salinity of 3.5 wt%. In electrolyte solutions, gas hydrate formation is controlled by water activity [7]. As a result, it is reasonable to think that sediment affects hydrate formation through pore water. The interaction of water with mineral surfaces has been observed for water with silica or clay [8, 9, 10], resulting in the formation of bound water layer at mineral surface.

No doubt the amount of bound water has is closely related to the specific surface area of silica or clay. As the bound water is not available for hydrate formation, less water can be converted into hydrate when the specific surface area is large. Thus a relationship between the degree of conversion of water into hydrate and the specific surface area can be expected.

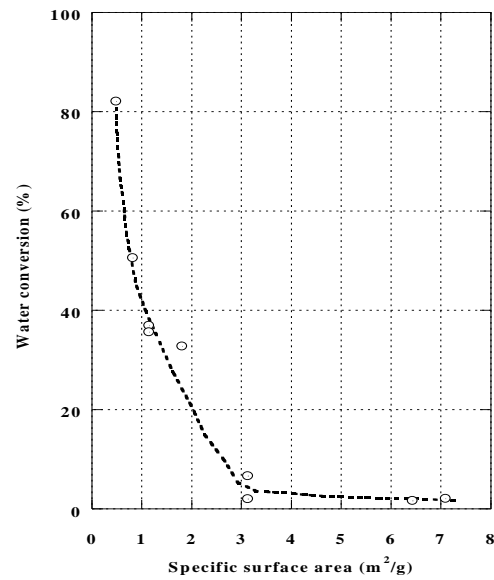


Figure 3. The relationship between the degree of conversion of water into hydrate in sand-kaolinite mixture.

As shown in Figure 3, a close relationship between the degree of water conversion and the specific surface area can be easily recognized with the sand-clay mixtures tested: there is less water converted into hydrate in the sample with the larger specific surface area.

Based on the above results, the observed particle size and clay effects on hydrate saturation result from the difference in specific surface area of the sediment.

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 water conversion to hydrate in a sediment decreases dramatically with the increase in clay content,
- 3) Fundamentally the water conversion to hydrate, or the saturation of gas hydrate, in

a sediment is controlled by its specific surface area.

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