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Influence Of Sediment Structural Properties And Their Dynamics In The Formation And Dissociation Of Methane Hydrates

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Abstract

Methane gas hydrate formation/ dissociation were investigated in sediments using a non- stirred reactor. The main focus of this study attributes to the dynamics of the sediments like clay and zeolite in methane hydrate formation. The pore scale habits of hydrates, hydrate formation techniques exerts a strong control on the macro scale physical properties of the sediments. An experimental study of methane hydrates is been performed at different sediment to water ratios(1-0.5),(1-0.8) of montmorillonite clay and (1-0.1) ,(1-0.2) of zeolite. The synthesis of hydrate is done using a 250ml auto clave at three different pressures typically at 85bars,70bars and 55bars. There is a significant change in the growth of methane hydrate both in Montmornillonite clay and zeolite before reaching to their saturation ratios.

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Key words: methane gas hydrate(MGH), Pore scale, dissociation points, Gas consumption.

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1. Introduction:

Gas hydrates are the three dimensional ice-like crystalline compounds, often found in nature. The four essential conditions for its 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. Gas hydrates exist as a stable solid phase in permafrost regions and in ocean-floor sediments around the globe where gas hydrates can naturally occur because of the conditions described above coexist [1]. Clay minerals are representative geochemical components comprising sediments and possess pores that can cause a confining effect on the gas to water system and change the properties of the confined gas hydrates[2–6]. The Previous experimental studies by Guggenheim et al. Suggest that methane hydrate structures can be stably formed in interlayer when the interlayer distance is 2.2 nm (a size that includes a lattice of methane hydrate)[2]. This study includes the dynamics of the sediment as well as an experimental method to investigate the mechanism of the hydrate formation and the effect of structural properties of sediments like clay and zeolite on hydrate formation and dissociation.

2.1 Experimental setup:

Hydrates of methane were formed in the pressure cell of volume 250ml in a non stirred autoclave apparatus .The cell was immersed in the temperature controlled water bath and a platinum thermometer was used to measure the temperature. The synthetic montmornillonite clay (44.17nm) and Zeolite (35.08nm) powders were obtained from Intelligent Materials Pvt. Ltd. (Nanoshel – www.nanoshel.com) and were used as they were (in their own form) after heating them to 100°C for 24hrs. To make them hydrophobic/ hydrophilic no special coatings were applied on to the clay and zeolite nano powder surface and were prepared in neutral pH conditions. The total setup is maintained at three different pressures of 55bars, 70 bars and 85bars. While cooling, the temperature was maintained for about 48 hours and 72 hours while warming .Then both the phases of gas and hydrate were observed.

1.1. Table:1 Percentage of yield and dissociation points:

Sample	sample to water ratio	Percentage of Yield(for 90%)	Td,Pd
Montmornillonite clay(44.17nm)	(1-0.5) 8.5Mpa	39%	282.15K,5.21Mpa
	(1-0.5) 7.0Mpa	47%	282.25K,6.34Mpa
	(1-0.5) 7.0Mpa	70%	285.05K,8.02Mpa
	(1-0.8) 8.5Mpa	10%	280.88K,5.02Mpa
	(1-0.8) 7.0Mpas	14%	283.70K,6.69Mpa
	(1-0.8) 5.5Mpa	17%	284.25K,7.61Mpa
Zeolite(35.08nm)	(1-0.1) 8.5Mpa	88%	280.90K,5.16Mpa
	(1-0.1) 7.0Mpa	99%	281.98K,6.42Mpa
	(1-0.1) 5.5Mpa	108%	283.95K,7.88Mpa
	(1-0.2) 8.5Mpa	4%	280.55K,4.94Mpa
	(1-0.2) 7.0Mpa	8%	282.85K,6.62Mpa
	(1-0.2) 5.5Mpa	13%	284.35K,7.85Mpa

Table 2 : Structural properties using BET studies:

Sample	Density of the sample	Total Pore volume(cm ³)	Average pore diameter(A)	Specific Surface area(As) m ² per gm	% of porosity(ϕ)
Montmornillite clay(44.17nm)	1.68	0.015cc/g	68.85 Å	9.007m ² /g	2.60%
Zeolite(35.08nm)	2.1	0.027cc/g	131.08 Å	8.377m ² /g	5.80%

2.2 Results and Discussions:

The methane gas consumption experiments were carried out in order to have a better understanding of the sediment behaviour during methane hydrate formation. The saturation degrees of water and changes in dissociation of gas hydrate were noted. The Figure 1 shows the cooling / warming curves for the methane hydrate system with clay and Zeolite at different water ratios . The observed P - T relationship for methane + sediment + pure water system can be approximated to the ideal gas law during a continuous cooling or warming cycle (as shown in Figure 1). However, during the dissociation there was a small shift towards higher temperatures compared to the SI Phase boundary equilibrium curve. This Shift is observed at different water ratios for both type of sediments , clay and zeolite at all the three pressures as shown in fig 2. This shift in the phase equilibrium points indicate that these sediments behave like good thermodynamic promoters which is similar to the results obtained by Nam-Jin Kim, Sung-Seek Park et .al.[7]. However the formation kinetics and overall hydrate conversion in porous sediments are also investigated in this study. Lin et al.[8] and Sun et al. [9] experimentally showed that an anionic surfactant could play an important role in expediting the formation of methane hydrate [8,9]. It is more evident from figure [yield pt curve]1 that MGH formation in association with clay and zeolite nano particles requires no such vigorous mechanical stirring and the MGH conversion is also significantly large (as seen from a huge pressure drop) in the preceding ratios of water. Table 1 shows that the amount of methane gas consumed in hydrate formation and total MGH yield in these experiments is decreasing as the water ratio is increasing in these sediments. These conclusions are relevant to our previous laboratory studies for silica matrix [10].Our experiments in lab showed that the formation kinetics is faster for the water-saturated systems. Also, there is no significant change in the formation kinetics for water-depleted systems which are in good agreement with the present experimental results of

sediments[10]. This might be due to the dynamics of the sediments inside the autoclave during the process of hydrate synthesis. As the hydrate preferentially forms at the contacts of the particles and stiffens the sediment framework, the studies on the strength, stiffness and the porosity reflect in the loss of sediment strength on hydrate dissociation and destruct the clay structure due to the inter particle electric repulsion which was already reflected in the previous literature studies[11]. In order to form the hydrate in clay for the former ratio, typically at 5.5mpa, 7mpa and 8.5 mpa the formation temperature changes from 275.1k,279.7k to 281.9k.Hence the time for growing the hydrate increases slightly. Further, it also might be for the reason that the growth of the hydrate increases at higher pressures as the hydrate yield is high.

The absolute amount of methane gas storage is remarkably low in water-depleted systems because the porous structure of the matrix is partly saturated with the water molecules. However, in a water-rich system, the hydrate conversion factor decreases and the kinetics are comparatively slower[11].It is well-known that the formation of the hydrate mostly occurs at the water and gas interface, and in the case of water in sediments, the hydrate formation was kinetically promoted because of an increase in methane consumption with time for different sediments with different water ratios. Once a certain amount of water converts to hydrates, it forms a sufficiently thick layer over the water phase and, hence, acts as a significant mass-transfer barrier for further hydrate growth; the subsequent conversion is diffusion-controlled [12, 13]. However, controversy exists whether it is the transport of the guest or the host (water) molecule through the crystal film that controls further hydrate growth. Recent high-resolution confocal Raman spectroscopy [14] has provided direct evidence for the mobility of H₂O molecules through the hydrate film, and thus the hydrate growth is controlled by the diffusion of water molecules. To use the hydrates for methane gas storage and transportation applications, it is important that the absolute gas amount trapped in hydrates must be high and at the same time, the total weight (combined weight of hydrate and matrix material) of the system should be low; i.e., the hydrate carrying porous medium must be saturated/supersaturated with water, so that most of the water is converted into hydrates[10]. Earlier reports showed that the hydrate yield is elevated only when the pores are moderately saturated with water[15]. Therefore, the amount of gas stored in such a system is less because of the higher matrix/water ratio. Recently, it was shown that use of dry water[16] or activated carbons[15-19] could be advantageous for improving the water/matrix ratio thereby, the hydrate yields (absolute methane carrying capacity)are more.

2.3 Effects of particle size:

The effects of the grain size of pure methane hydrates on its dissociation process have already been reported and the dissociation rate for smaller grains was much faster than larger grains (Takeya et. al., 2005). On contrary, the methane hydrates formed in glass beads of different sizes dissociated in the temperature range 200 – 260 K (Hachikubo et. al., 2011). The hydrates within larger pores (several tens microns to 100 μ m) dissociated quickly and those in smaller pores (less than a few microns) were dissociated in two stages and the final dissociation temperature

was around 260 K (Hachikubo et. al., 2011).Whereas, we could not find huge variation in the dissociation temperatures in case of clay and zeolite (nano powders) for both the water ratios with different pressures. However, we could find 30-40% increase in the yield in case of zeolite nano powders compared to clay as the structural properties like cementation of grains by gas hydrate has large effects on shear modulus but few effects on the volume modulus[11]. The cementation contribution to shear strength of clay or zeolite decreases with increase in specific surface area of soil minerals. The specific area , pore density and pore volume calculations are experimentally verified by using BET studies as shown in table 2.

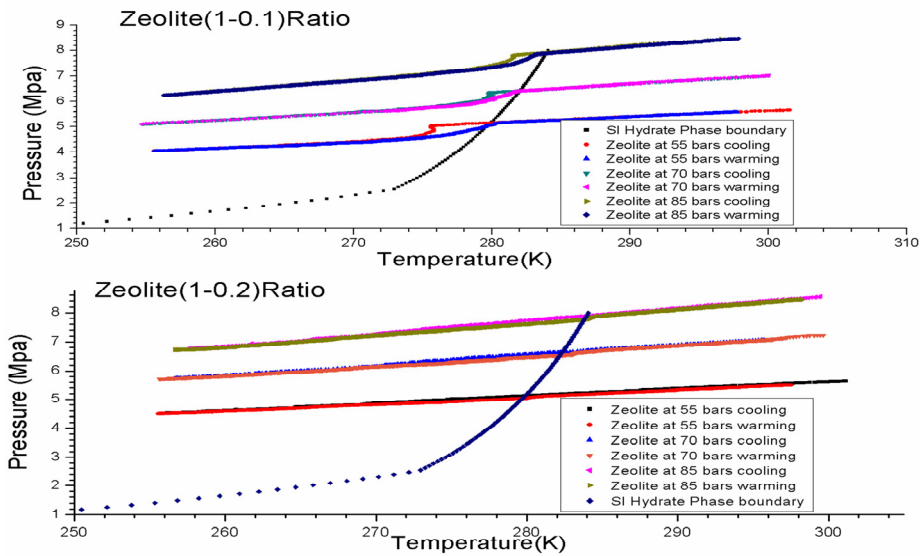


Figure :1 (PT traces of methane hydrate with zeolite at different pressures).

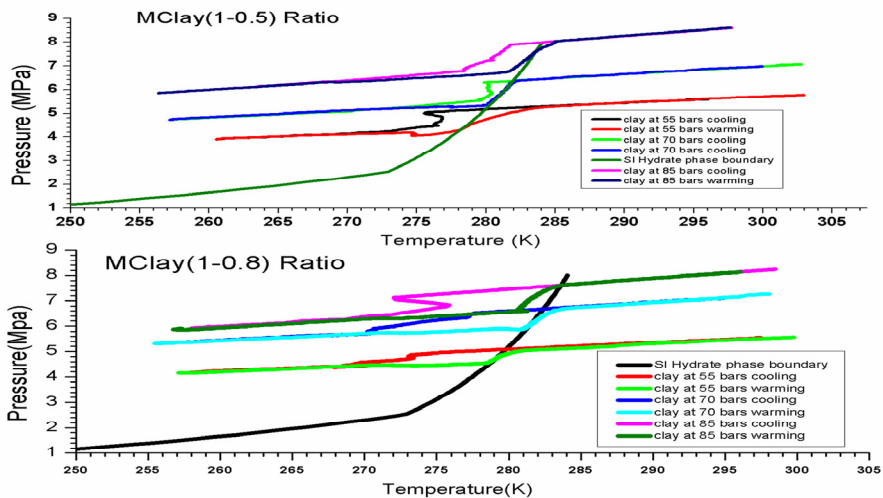


Figure:2 (Dissociation points of clay and zeolite with SI hydrate phase boundary curve)

2.4 Conclusions:

Storage of methane hydrate using sediments like clay and zeolite of nano powders with a variable amount of water was investigated. Even though, there is no significant increase or decrease in the formation time in clay and zeolites for partial water systems in two ratios. The dynamics of these porous media giving rise to increased hydrate yields compared to bulk systems are similar to our previous experimental results, which was the motivation for these conclusions in sediments. In addition to this, the structural properties like porosity, pore diameter, pore volume, surface area at low temperatures typically at 77k were examined using BET studies.

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