

Thermal and Structural Properties of the Nano Sediment Suspensions in the Synthesis of Methane Hydrates

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Abstract

Comparative studies have been carried out on mechanical properties of the sediments enhancing the formation and dissociation of methane hydrates. Porous media significantly influence the rate of hydrate formation by reducing the chemical barrier, where zeolites are the micro porous minerals. It was observed that the gas consumption was slightly greater in zeolite compared to montmorillonite clay for the first ratios before reaching to the saturation ratios. This paper also tells that, at constant dissociation rate the enthalpy or the amount of heat release of methane gas is increasing for the higher pressures at two water ratios both in clay and zeolite sediments, giving rise to effectiveness in enhancing and expediting the methane hydrate formation which is an ultimate source for energy demanding applications. In addition to this, we have observed a slight reduction in the permeability for clay sediment giving an evidence for the hydrate growth.

Key words: Gas hydrate, sediment, Porosity, permeability

INTRODUCTION

A comparative studies has been carried out on mechanical properties of the sediments enhancing the formation and dissociation of methane hydrates. Porous media significantly influence the rate of hydrate formation by reducing the chemical barrier, where zeolites are the micro porous minerals. It was observed that the gas consumption was slightly greater in zeolite compared to montmorillonite clay for the first ratios before reaching to the saturation ratios. This paper also tells that, at constant

dissociation rate the enthalpy or the amount of heat release of methane gas is increasing for the higher pressures at two water ratios both in clay and zeolite sediments, giving rise to effectiveness in enhancing and expediting the methane hydrate formation. In addition to this, we have observed a slight reduction in the permeability for clay sediment giving an evidence for the hydrate growth.

Materials:

The synthetic montmorillonite 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). The sediment sample was dried at 120C for 24 hours to remove the pore waters. The required amount of sediment, and degassed ultra-pure water were measured by using Metler Toledo (AB104-S) accurate analytical balance.

Experimental Setup:

Hydrates of methane were formed in the pressure cell of volume 250ml using 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 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.

Dynamics of the sediment:

The saturation degrees of water and gas change with the dissociation of GH. The structural and mechanical properties of the sediments such as the porosity and permeability change accordingly. The formation of GH in sediment is affected by the pore scale, the physical and chemical characteristics of the grain surface, grain series, grain shape, permeability etc., which is obviously different with that of cubic GH. Different laboratory methodologies for synthesizing methane hydrate can result in different hydrate habits and hence different physical properties for identical sediments with equal hydrate saturations. These laboratory methods produce different pore-scale growth habits [2, 3]. The hydrate growth rate is limited by the concentration of hydrate former in the water. The dissolved gas method is limited to form hydrate saturations below 60%–70% for which water remains a percolating phase and can continue to circulate. Soil grains are mixed with a limited amount of water (or by introducing the methane as bubbles into the fully water saturated soils) and packed to form a partially water-saturated sediment. This method leads to preferential hydrate formation at contacts and stiffening of the sediment framework [4]. In this paper, by using this partial water saturation method, methane hydrate preferentially forms at contacts of particles and stiffens the sediment framework (cementation-type)[4].

Enthalpy :

According to Sloan [1] to a first approximation the dissociation enthalpy is a function of the following factors: the hydrogen bonds making up the lattice, the cavity occupation, and the guest size. About 80% of the total dissociation enthalpy is due to the strength of the water hydrogen bonds[1] The dissociation enthalpy is defined as the enthalpy change to decompose the gas hydrate. From the fig1 and 2 enthalpies are estimated from phase equilibrium and thermodynamic data using the Clausius-Clapeyron equation to relate pressure, P; temperature, T; enthalpy, ΔH ; and compressibility,

$$\frac{d \ln P}{d(1/T)} = \frac{-\Delta H}{ZR}$$

where R is the ideal gas constant. The validity of this method is contingent upon negligible changes in compressibility. ΔH depends on the guest molecule but is primarily controlled by the number of hydrogen-bonded water molecules[1].

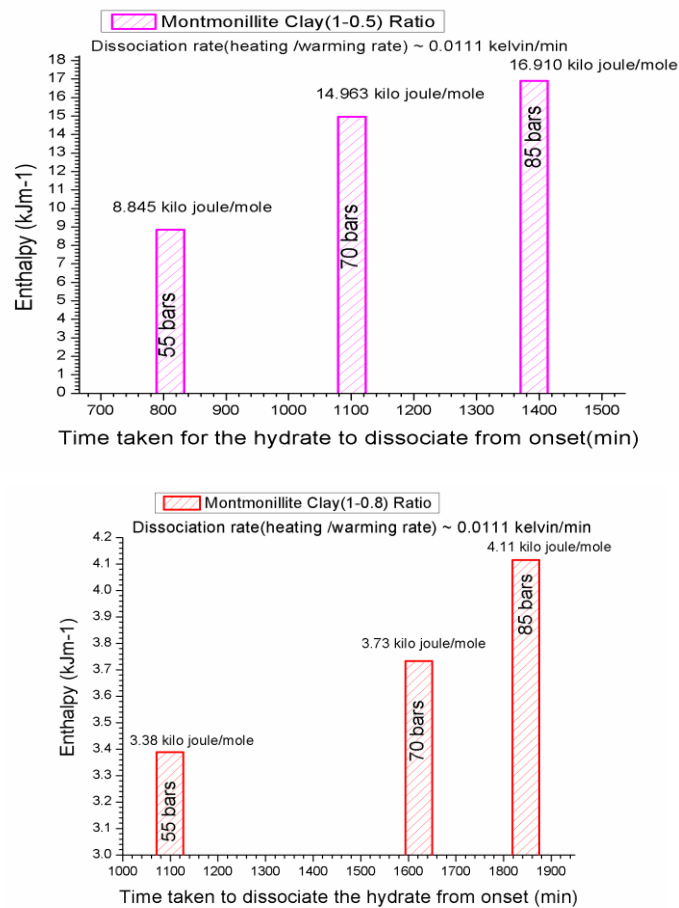


Figure 1. Enthalpy for clay at different water ratios with different pressures.

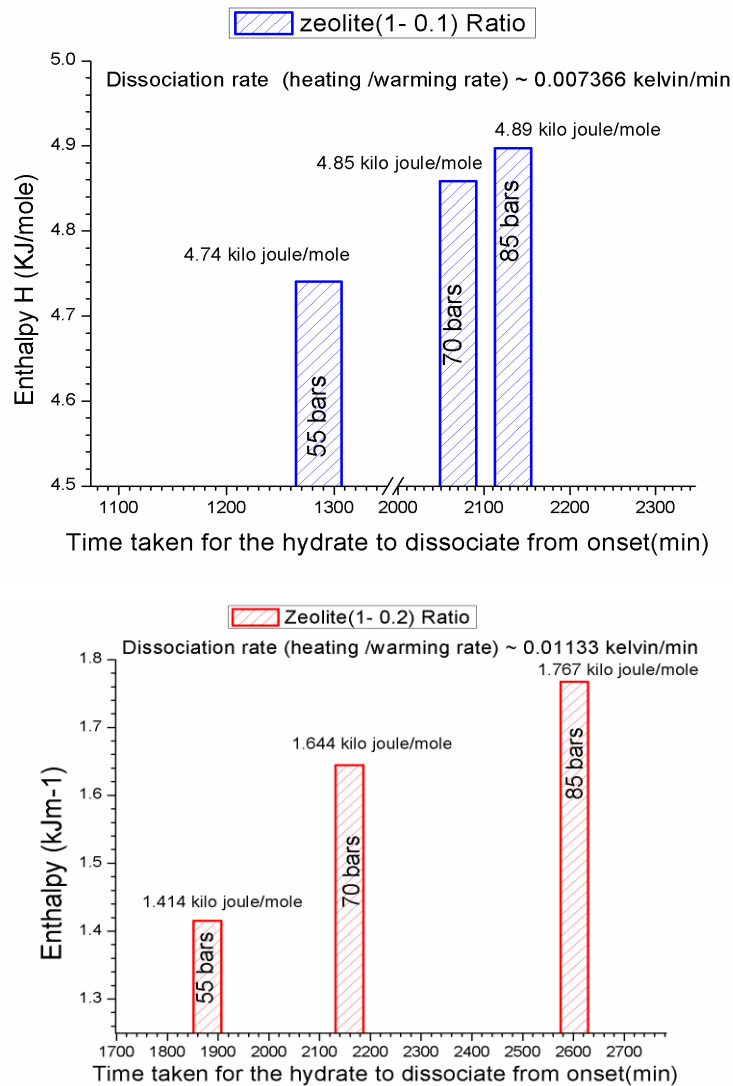


Figure 2. Enthalpy for zeolite at different water ratios with different pressures.

Porosity measurements:

In most sedimentary systems including sediments like clay and zeolites, fluid transport occurs through a heterogeneous permeability network that can be represented as a combination of fractures and a porous medium[5]. Generally, hydrate accumulation and permeability clogging occur at a faster rate in the porous medium than in the fractured system. So inversely, the decrease of permeability lowers or even stops the formation of gas hydrate [6-8] by reducing the pore size and changing the pore shape. Pore-filling hydrate reduces the permeability more significantly than mineral coating hydrate [9]. Generally, the effective absolute permeability does not decrease significantly until hydrate saturation reaches ~40%. Beyond that point the permeability decreases rapidly as hydrate saturation increases, and becomes nearly zero before the pore space is fully

filled with hydrate [10]. Absolute permeability was measured by water flow and calculated by Darcy’s law as shown in the table 2. For simplicity, the permeability is mostly assumed as the function of the porosity and the specific surface area, for an example, the model presented by [11]

$$k = \frac{\phi^3}{2A_s^2}$$

in which ‘k’ is the absolute permeability, ‘ ϕ ’ is the porosity, ‘A’ is the specific surface area.

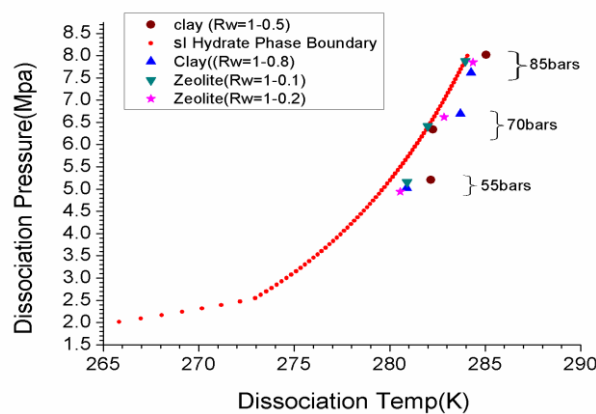


Figure 3. Dissociation points of methane hydrates for clay and zeolites at different ratios of water with different pressures

Table :2 (structural properties of clay and zeolite)

Sample Name	Method	Pore volume cm ³	Density of the sample	Total volume (for 1gm mass of a sample)cm ³	% of porosity(ϕ)	permeability (darcy law) $k=\phi^3/2(A_s)^2(/m^2)$
Montmorillonite Clay (44.17nm)	BET at low temperature (~77k)	0.0155	1.68	0.595	2.6 %	1.08 X 10 ⁻¹⁵
	Pycnometer at room Temp	-	-	-	3.3 %	-
Zeolite (35.08nm)	BET at low temperature (~77k)	0.0274	2.10	0.47	5.8 %	1.38 X 10 ⁻¹⁴
	Pycnometer at room Temp	-	-	-	3.6 %	-

Experimental Results:

Previous studies have shown that the thickness and porosity of the nan fiber mats can be controlled by changing the deposition rate of nano fibers [12,13].In this present work we have done a comparative study on the porosity using pycnometer and BET analysis.

Though use of pycnometer for measuring the pore volume of porous materials may not be new but we believe that use of pycnometer for measurement of porosity of clay and zeolite is a new method. The advantage of pycnometry for the porosity measurement of nano fibers has also been discussed in the literature studies[14]. From the fig 1 & 2, we observed that at a constant dissociation rate the enthalpy during the dissociation is increasing significantly in both type of clay and zeolite sediments at three pressures with different water saturation ratios, which is a good sign for hydrate growth (From table 1). In addition to this from fig 3, we found that the dissociation points are shifting to higher temperatures indicating like a good thermodynamic promoter on using these sediments. Compared to clay, growth of hydrate in zeolite is better as it is more permeable with respect to its aluminum frame work (From table 2). Reduction of permeability of clay as shown in the table 2, is an evidence for cementation of the hydrate and blocks the water to penetrate after reaching to the second ratio. The results show that the rapid cat ion exchange process in montmorillonite can influence macro scale parameters, such as permeability and strength, which can contribute to changes in local pressure conditions [15].

Table :1(Percentage of hydrate yiled for zeolite & clay)

Sample	sample to water ratio	Percentage of Yield(for 90%)
Montmorillonite clay(44.17nm)	(1-0.5) 8.5Mpa	39%
	(1-0.5) 7.0Mpa	47%
	(1-0.5) 7.0Mpa	70%
	(1-0.8) 8.5Mpa	10%
	(1-0.8) 7.0Mpas	14%
	(1-0.8) 5.5Mpa	17%
Zeolite(35.08nm)	(1-0.1) 8.5Mpa	88%
	(1-0.1) 7.0Mpa	99%
	(1-0.1) 5.5Mpa	108%
	(1-0.2) 8.5Mpa	4%
	(1-0.2) 7.0Mpa	8%
	(1-0.2) 5.5Mpa	13%

CONCLUSIONS

The studies of methane hydrate growth on using sediments like MClay and zeolite nano powders and their permeability variations with different techniques has being studied. When compared to the second ratios of sample to water, the growth of the methane hydrate on usage of zeolite has increased to 20-30% compared to clay sediment in the preceding ratio. We have shown that the type of interlayer cation influences macroscopic properties such as permeability, Porosity in sediments within the effective pressure range of 5.5MPa to 8.5 MPa.

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