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A Review on Synthesis of Methane Hydrates and the Thermal and Structural Properties of Nano Sediment Suspensions

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Abstract

Comparative investigations on the mechanical characteristics of sediments facilitating the development and dissociation of methane hydrates have been conducted. Porous media, such as zeolites, have a major impact on the pace of hydrate formation by lowering the chemical barrier. The gas consumption in zeolite was somewhat higher than in montmorillonite clay during the initial ratios before reaching saturation ratios. This paper also describes how, at constant dissociation rates, the enthalpy or amount of heat released by methane gas increases for higher pressures at two water ratios in clay and zeolite sediments, resulting in increased effectiveness in enhancing and expediting methane hydrate formation, which is an ultimate source for energy demanding applications. In addition, we discovered a modest decrease in the permeability of clay sediment, indicating the presence of hydrate development.

Keywords: *- Porosity, Permeability, Gas hydrate, sediment*

INTRODUCTION

A comparative study on the mechanical characteristics of sediments increasing the development and dissociation of methane hydrates was conducted. Porous media, such as zeolites, have a major impact on the pace of hydrate formation by lowering the chemical barrier. The gas consumption in zeolite was somewhat higher than in montmorillonite clay during the initial ratios before reaching saturation ratios.

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This study also states that, under continuous

The dissociation rate, enthalpy, or quantity of heat released by methane gas, is rising for higher pressures at two water ratios in clay and zeolite sediments, indicating success in boosting and speeding methane hydrate formation. In addition, we discovered a modest decrease in the permeability of clay sediment, indicating the presence of hydrate development.

MATERIALS:

Intelligent Materials Pvt. Ltd. (Nanoshel - www.nanoshel.com) provided the synthetic montmorillonite clay (44.17nm) and Zeolite (35.08nm) powders, which were employed as is (in their own form). To eliminate pore fluids, the sediment sample was dried at 120°C for 24 hours. The needed quantity of sediment and degassed ultra-pure water were measured using a precise analytical balance from Metler Toledo (AB104-S).

Experimental Setup:

Methane hydrates were produced in a 250ml pressure cell using a non-stirred autoclave device. The cell was submerged in a temperature-controlled water bath, and the temperature was measured with a platinum thermometer. The whole configuration is kept at three distinct pressures: 55bars, 70bars, and 85bars. The temperature was kept stable for 48 hours during cooling and 72 hours when warming. The phases of gas and hydrate were then detected.

Dynamics of the sediment:

With the dissociation of GH, the saturation degrees of water and gas change. Sediment structural and mechanical qualities like as porosity and permeability alter as a result. The pore size, physical and chemical properties of the grain surface, grain series, grain shape, permeability, and other factors influence the development of GH in sediment, which is plainly different from that of cubic GH. For similar sediments with equivalent hydrate saturations, different laboratory procedures for generating methane hydrate might result in distinct hydrate behaviours and hence varied physical characteristics. Different pore-scale growth behaviours are produced by these laboratory procedures [2, 3]. The concentration of hydrate former in the water limits the pace of hydrate development. The dissolved gas approach is restricted to hydrate saturations of less than 60%-70%, for which water stays in a percolating phase and can circulate. Soil grains are combined with a little quantity of water (or introduced as bubbles into

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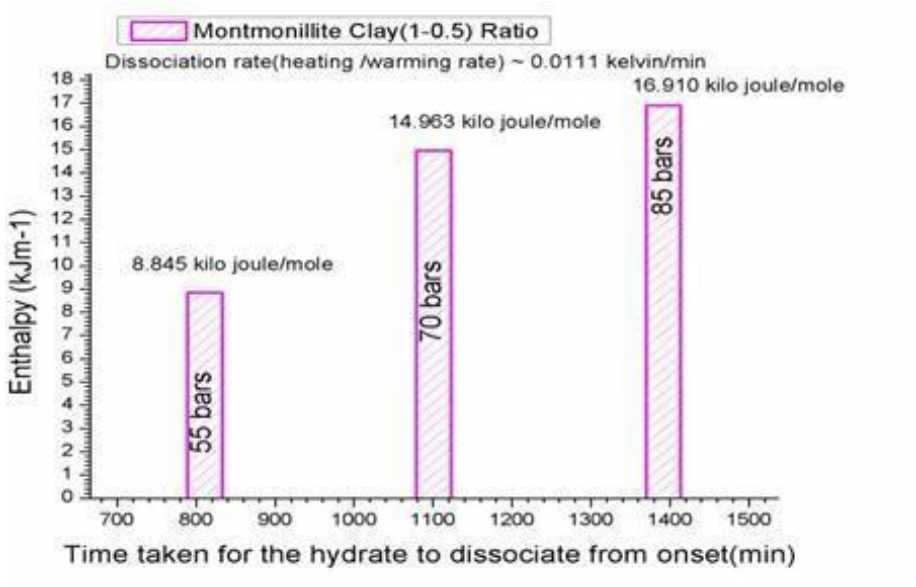
completely saturated soils) and compacted together to produce a partly water-saturated sediment. This approach causes preferential hydrate formation at contact points and stiffens the sediment structure [4]. Using this partial water saturation approach, methane hydrate develops preferentially at particle interactions and stiffens the sediment structure (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 fig1and 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,

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

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].



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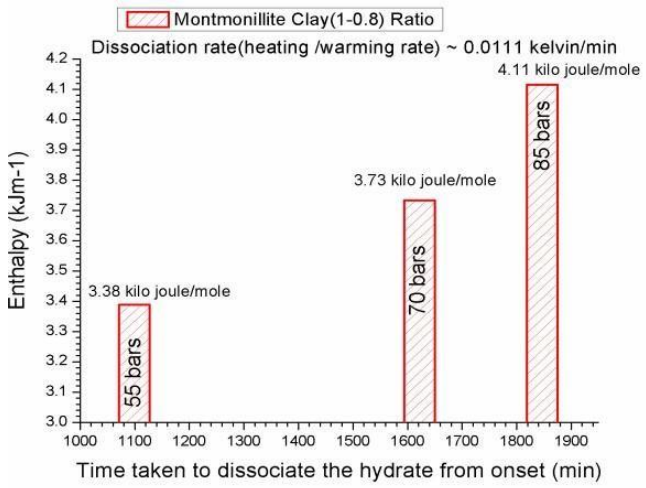


Figure 1. Enthalpy for clay at different water ratios with different pressures

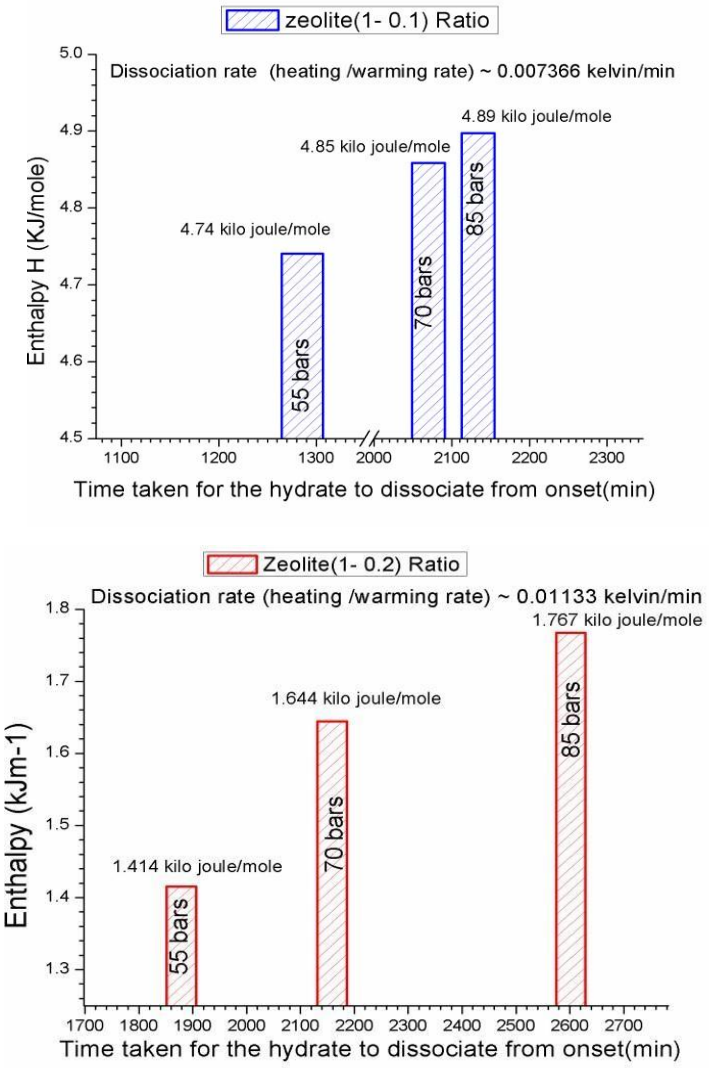


Figure 2. Enthalpy for zeolite at different water ratios with different pressures

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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 surfacearea.

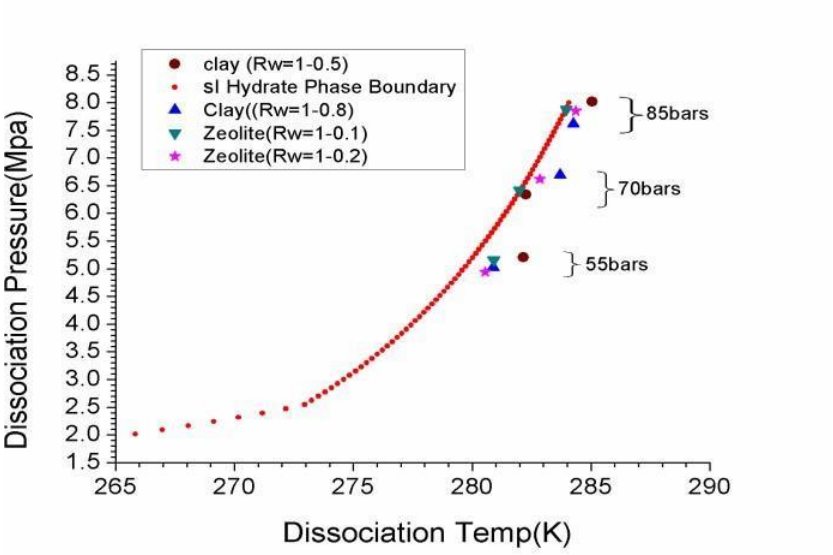


Figure 3. Dissociation points of methane hydrates for clay and zeolites at different ratios of water with different pressures

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Table: 1 (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) $k=\phi^3/2(As)^2(/m^2)$
Montmorillonite Clay (44.17nm)	BET at low temperature (~77k)	0.0155	1.68	0.595	2.6 %	1.08×10^{-15}
	Pyconometer at room Temp	-	-	-	3.3 %	-
Zeolite (35.08nm)	BET at low temperature (~77k)	0.0274	2.10	0.47	5.8 %	1.38×10^{-14}
	Pyconometer at room Temp	-	-	-	3.6 %	-

EXPERIMENTAL RESULTS

Previous research has demonstrated that adjusting the deposition rate of nano fibres may influence the thickness and porosity of nan fibre mats [12,13]. In this paper, we conducted a comparative research on porosity utilising a pycnometer and BET analysis.

Though the use of a pycnometer to measure the pore volume of porous materials is not novel, we feel that using a pycnometer to measure the porosity of clay and zeolite is. The advantages of pycnometry for measuring the porosity of nanofibers have also been explored in the literature[14]. Figures 1 and 2 show that at a constant dissociation rate, the enthalpy during dissociation increases considerably in both types of clay and zeolite sediments at three pressures with varied water saturation ratios, indicating hydrate formation (From table 1). Furthermore, we discovered in fig 3 that the dissociation points are migrating to higher temperatures, showing that employing these sediments is a good thermodynamic promoter. In comparison to clay, hydrate growth in zeolite is superior since it is more permeable due to its aluminium framework (From table 2). The reduction in clay permeability, as indicated in table 2, provides evidence for hydrate cementation and limits water penetration after reaching the second ratio. The findings indicate that the quick cat ion exchange process in montmorillonite can impact macro scale

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properties like permeability and strength, which can contribute to changes in local pressure conditions [15].

CONCLUSIONS

The formation of methane hydrates on sediments such as MClay and zeolite nano powders, as well as their permeability changes using different procedures, has been examined. As zeolite was used instead of clay sediment in the previous ratio, the development of the methane hydrate increased by 20-30% when compared to the second ratios of sample to water. We demonstrated that the kind of interlayer cation effects macroscopic characteristics such as permeability and porosity in sediments with effective pressures ranging from 5.5 MPa to 8.5 MPa.

Table: 2 (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%

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