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Research paper

Experimental investigations of methane hydrate in sediment suspensions

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Abstract

Methane hydrate structural stability and formation, were studied in water suspensions with synthetic clay (44.17nm),SiO2(60.62nm) and zeolite (35.08nm) at different weight percentages (1wt%,10wt%,20wt%) in isochoric method using stirred autoclave. The for- mation kinetics in these sediments greatly differs from those of the bulk hydrate owing to surface and capillary effects in the pores. It has been confirmed that hydrate formation in confined pores is severely restricted due to increased inner capillary pressure. Further- more in prin- ciple , the clay particles suspended in water play a negative role in structuring the crystalline hydrate .More specifically, even though the addition of clay enhances the hydrate yield insignificantly, from our results, the addition of sediments did not affect the phase equilibrium much because water exists in excess around clay particles and therefore the hydrate formed in the bulk water phase is much more dominant than that in the pores.

Keywords: *Gas Hydrates; Methane; Phase Equilibrium.*

1. Introduction

Gas hydrates are crystalline compounds formed by water as a host molecule and the guest molecule is typically a gas or liquid at high pressures (typically more than 6mpa) and low temperatures (slightly below room temperature).Three distinct structural fami- lies, structures I, II, and H are known showing distinct size and shape of polyhedral cages that capture the guest molecules accord- ing to the structures. In addition to favorable temperature and pres- sure conditions, water salinity changes the stability conditions of gas hydrate in marine sediments

2. Experimental method

2.1. Materials

Porous sediments with different weight percentages of Clay, SiO2 and Zeolite were used in the study. The sediments were supplied by intelligent materials Pvt. Ltd (Nanoshel).The samples were dried (at 120-150 oc for 6 -8 hr) to remove the pore waters. The required amount of the sediment was measured by using Metler Toledo (AB104-S) accurate analytical balance. The distributions of pore volume pore diameter and specific surface area was de- termined by BET studies also listed in table 2.

2.2. Experimental apparatus

The main part of the apparatus is an SS-316 cylindrical ves- sel, which can withstand the pressures up to 10MPa and vol- ume of the vessel is 100mL.A stirrer with variable speed was installed in the vessel to agitate the fluids. The top stirrer was kept-on at 500 rpm for the experiments in stirred reactor for the entire duration (~18hrs). Cold fluid (water+glycol mix- ture) was circulated around the vessel with the help of Lab Companion (RW-0525G) circulator, to maintain the tempera- ture inside at a desired level. A platinum resistance thermom- eter (Pt100) is inserted into the vessel to meas- ure the temper- ature with an accuracy of ± 0.2 K. The pressure in the vessel was measured with a WIKA pressure transducer (WIKA, type A-10 for pressure range 0 to16 MPa).The cell was then pres- surised with methane gas to a desired level using Tele- dyne ISCO Syringe pump (Model-100DX). After obtaining temperature and pressure stability (far above the hydrate for- mation region), then the valve inline connecting the vessel and the ISCO pump was closed. Subsequently, temperature was slowly decreased to form hydrate in the vessel was de- tected by pressure drop. The experi- ments were carried in iso- choric process. Once the hydrate for- mation was completed, then the temperature was increased in steps just above the hydrate-forming region, hydrate crystals partially dissociate, thereby substantially increasing the pressure. Conse- quently, as the temperature is increased further the system reaches to a point at which the slope of pressure-temperature data plot changes sharply was considered to be the point at which all hydrate crystals have dissociated. In this way, a pressure temperature dia- gram was obtained for each experimental run, from which we de- termined the hydrate formation and disso- ciation pattern. The pres- sure and temperature were recorded at each 60 sec interval using the data acquisition system.

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Table 1: Yield and Formation Kinetics of Methane Gas Hydrate for Different Sediments at Different Concentrations

Sediment used	Number of moles of gas	% of yield	Kinetics(90% Avg from two best cycles)
Pure water (30ml)+ CH4 6g clay	77. 91.5 3	26.68 ±1. 31.56 ±1 59	77.5min 170min
3g clay	85	29.32 ±1	330min
0.3g clay	96	44.06 ±7	510min
6g Zeolite	109.5	37.77 ±3.17	345min
3g Zeolite	102	35.19 ±0.97	280min
0.3g Zeolite	56	19.32 ±5.3	135min
6g SiO2	93.3	36.26 ±2.09	125min
3g SiO2	86.5	29.32 ±1	90min
0.3g SiO2	93	32.08 ±2.1	180min

3. Results and discussion

3.1 Hydrate formation

Hydrates are generally stable at high pressures and low tem- peratures but can decompose easily into water and gas outside their stable region. In our present experiments, 30mL of water is injected in to the cell through an injector and cooled to 270.15K.The reactor was pressurized by methane gas for the pres- sure range of 3-7MPa. These conditions were kept constant for several hours to allow complete hydrate formation. Once the hydrates were formed, the reactor temperature is increased slowly and hydrate starts dissociating showing the raise of pressure. The formation of hydrate in sediments shows that the phase equilibri- um points are located to the right of the phase boundary curve fig 2, which is in similar to the results obtained by Nam-Jin Kim, Sung-Seek Park et .al. [1]. However the formation kinetics and overall hydrate conversion in porous sediments are also investi- gated in this study. Lin et al. [3] and Sun et al. [5] experimentally showed that an anionic surfactant could play an important role in expediting the formation of methane hydrate [3], [5]. Seo et al. [6] and Ryu et al. [2] examined the roles of porous silica gels and nano-materials in natural gas storage. Addition of nano SiO2 powder promoted an increase in the gas water interfacial surface area by forming a dispersed water phase at ambient temperature [7]. Some researchers studied the adsorption of methane using activated carbons, where a number of promising methods were reported on methane storage by physical adsorption [8–11]. The amount of gas consumed in case of 0.3g of clay was about 8-10% higher than in case of pure system as shown in table 1. There exists a gradual decrease in the amount of gas consumed in case of clay when more than 0.3g of clay is used (fig 1), which is in good agreement with additives [12], [13]. This might be because of agitat- ing effect got reduced and there by water to gas surface area decreases at more concentrations of clay, hence hydrate yield de- creases. which even has been reported by S. S. park et.al [13].

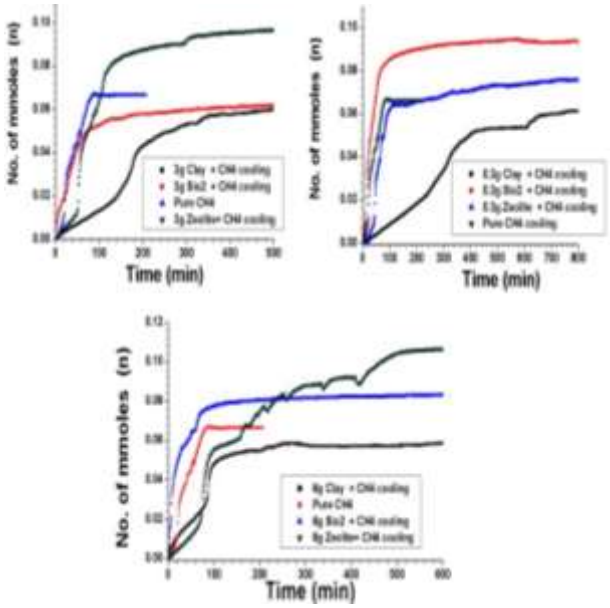

Fig. 1: Formation Kinetics of Methane Hydrate for Sediments.

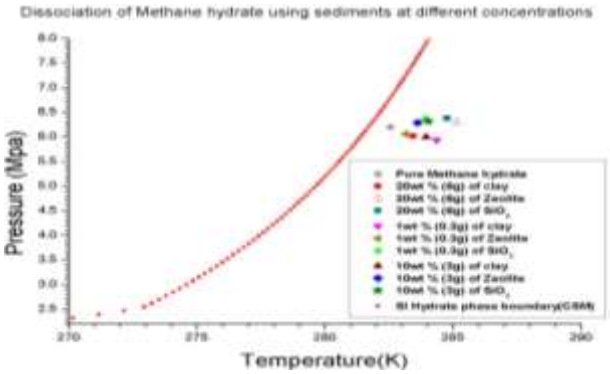

Fig. 2: Dissociation of Methane Hydrate Using Sediments.

Table 2: Physical Properties of the Sediments:

Property	Clay (44.17nm)	SiO_2 (60.62nm)	Zeolite (35.08nm)
Average pore Diameter (A)	68.850 Å	148.458 Å	131.082 Å
All pore diameter(A)	111.039 Å	330.066 Å	317.286 Å
Specific Surface Area	9.007 m2/g	335.724m2/g	8.377 m2/g
Total Pore Volume	0.015 cc/g	1.246 cc/g	0.027 cc/g

3.2. Analysis by using BET method of gas adsorption

Here, the physical adsorption of gas(nitrogen)molecules on a solid surface serves as the basis for the determination of its specific surface area using BET is as shown in table 2. In the BET theory, It is assumed that molecules can be adsorbed in second, Third….and nth layers, the surface area available for the nth layer Being equal to the coverage of the (n-1)th layer. Using BET stud ies it may again be noted that in the case of adsorption isotherms OF TYPE IV and V, there is not only formation of multi molecular adsorbed layers of the gas molecules, but also condensation of some of the gas molecules within the narrow capillary pores of the adsorbent. This latter phenomenon is known as capillary condensation of the gas.

4. Conclusions

The experimental data for the hydrate yield are in good agreement with the data in literature when we use different additives. Stirring effects the enhancement of hydrate yield in methane gas hydrates. It is observed that phase equilibrium points for these porous sediments are shifting towards right as shown in fig2, insignificantly In comparison with pure methane phase boundary curve. The amount of gas consumed during hydrate formation is found to be Increased in presence of additives by 8-10% compared to bulk System.

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