

THE FORMATION OF CARBON DIOXIDE HYDRATE IN SOLID SUSPENSIONS AND ELECTROLYTES

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ABSTRACT

Evaluation of host geologic sediment interactions with carbon dioxide is very important in sequestration strategies. The objective of the study is to experimentally investigate the effects of different soil mineral types on carbon dioxide hydrate formation. At isothermal, isochoric, and isobaric conditions, batch experiments were conducted with different types of solids (bentonite, kaolinite, nontronite, pyrite, and soil) and electrolytes (NaCl, KCl, CaCl₂, and MgCl₂) to measure carbon dioxide hydrate formation times. A 50 mL pressurized vessel was used for the experiment by bubbling gaseous CO₂ into the solid suspension. We observed that the formation time of carbon dioxide hydrate was dependent on the reactor temperature (273.4 K and 277.1 K) and types of solid and electrolyte. A clear peak was observed in the temperature profile of each experimental run and determined as the hydrate formation time. This is due to the initiation of the hydrate crystallization and latent heat release at the hydrate formation time. The temperature profiles vary significantly with respect to the types of solids and electrolytes. As crystallization initiates, peaks were observed at higher temperatures in pyrite and soil suspensions. The results showed that hydrate formation times for clay minerals in water were approximately twice and 10 times faster than that for pyrite and soil, respectively. The rates of gas consumption were able to be determined by the pressure monitoring. The kaolinite appeared to have the fastest gas consumption rate among the clay mineral suspensions, which was 2.4 times and 7.4 times faster than nontronite and bentonite, respectively. Results from these experiments seem to provide an insight on the formation and growth of carbon dioxide hydrate, once sequestered into the sea bed sediments under the deep sea environment.

Keywords: carbon dioxide hydrate, soil minerals, gas consumption rate, chemical interactions

NOMENCLATURE

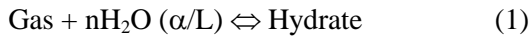
Mega-ohm-cm [MΩ•cm]
cubic centimeter [cm³]
grams [g]
Kelvins [K]

INTRODUCTION

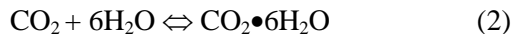
Clathrate hydrate formation is a natural phenomenon that occurs under high-pressure and low temperature conditions. These are crystalline compounds made up of small guest molecules

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physically trapped in host cavities shaped by hydrogen bonded water molecules [1-2]. The process provides an insight on the application to immobilization techniques of pollutant gases from combustion facilities into geological formations. The formation of gas hydrate is an exothermic equilibrium reaction and can be expressed by:



where the aqueous phase may be composed of ice, α , or liquid, L[3]. It has been proposed that instead of spewing out the off-gas wastes from combustion facilities and power plants, the off-gas should be collected, mixed with water under the appropriate hydrate forming conditions [4]. A common pollutant gas is shown below to illustrate the hydrate formation:



Studies have shown that several factors are involved in hydrate formation. Temperature, pressure and chemical potential gradient are commonly identified as driving forces in the nucleation of hydrates [2]. Chemical characteristics of electrolyte, natural organic matters, soil minerals, and biosurfactants, which are naturally found in geological formations have been specifically identified to have significant influences on the chemical potential gradient between the gas-water boundary layer and in turn, in the arrest or promotion of hydrate formation[5-7].

Sand and clays have been studied to have stronger interactions with water molecules in the hydrate formation. Clays have been known to aid in hydrate formations [5,7-8]. However, few studies have been conducted on the carbon dioxide hydrate formation in a system consisting of electrolyte, hydrate-forming gas, and soil minerals. No study has been conducted using pyrite and terrestrial soils in promoting hydrate formation. By means of varying different type of surfaces, we could further elucidate the hydrate formation mechanisms in host sediments. Evaluating the gas-rock-water interactions could facilitate our understanding in storage of CO_2 into geological formations.

In this study, we experimentally investigate the effects of different soil mineral types on carbon dioxide hydrate formation. At isothermal, isochoric, and isobaric conditions, batch experiments were conducted with different types of solids (bentonite, kaolinite, nontronite, pyrite, and soil) and electrolytes (NaCl , KCl , CaCl_2 , and MgCl_2) to measure carbon dioxide hydrate formation times. Moreover, we have correlated the hydrate formation with the solid surface chemical properties.

EXPERIMENTAL SET-UP

Experimental materials/apparatus

The gas hydrate former used in the experiment was a commercial 99.9% grade compressed CO_2 . Bentonite ($\text{Na}(\text{Al}, \text{Mg})_6(\text{Si}_4\text{O}_{10})_3(\text{OH})_2 \cdot n\text{H}_2\text{O}$, Kyoungju, Korea) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, Pusan, Korea) were obtained from Korea Bentonite Co. (Seoul, Korea) and Duckyu Ceramics (Sungnam, Korea), respectively. Nontronite ($\text{Na}_{0.3}\text{Fe}^{3+}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$, Cheney, Washington) and pyrite (FeS_2 , Zacatecas, Mexico) were purchased from Ward's International (New York, USA). Soil sample was collected from the subsurface at Korea Advanced Institute of Science and Technology, Daejeon, Korea.

The following chemicals used were reagent or higher grade chemicals: NaCl , CaCl_2 , MgCl_2 , KCl , and ethylene glycol. The gas, soil, soil minerals, and chemicals were used without further purification. An exact amount of electrolyte (NaCl , KCl , CaCl_2 , and MgCl_2) was added to deionized water ($18 \text{ M}\Omega \cdot \text{cm}$) to gravimetrically prepare 3.5% electrolyte solution. Soil and soil minerals (0.2 g of each solid) were added into 30 mL solutions containing the electrolytes to prepare the solid suspensions.

The schematic diagram for the experimental set-up is shown in Figure 1. The hydrate formation and dissociation experiments were conducted using a cylindrical 304 stainless steel pressurized vessel (50 cm^3) reactor. It has 2 tempered sight ports on opposite sides to allow visual observation during the hydrate formation and dissociation experiments. The vessel was immersed in a temperature-controlled liquid bath maintained by a

refrigerated liquid circulator (Model WCL-212, Daihan, Korea). The bath liquid was a mixture of ethylene glycol and tap water. The pressure of vessel was continuously monitored by a pressure transducer. The pressure transducer was located at the upper part of the vessel to measure the headspace pressure. The reaction temperature in the vessel was monitored by temperature sensor. The thermometer sensor was installed laterally to the pressurized vessel and was purposely located at the gas-water interface. Pressure-time and temperature-time readings were recorded with an Agilent data-acquisition system.

Experimental procedures

CO₂ hydrate formation experiments were conducted under isochoric and isothermal conditions. Monitoring of hydrate formation conditions and measurement of hydrate formation time were conducted by following the experimental steps below. The reaction vessel was filled with 25 - 30 mL of solid suspension with 3.5% electrolyte leaving 20 - 25 mL of headspace. The vessel was placed into a cold bath temperature condition (273.4 K or 277.1 K). When the vessel temperature has reached equilibrium, the vessel was purged with CO₂ to remove air from the headspace and dissolved air in the suspension. The vessel was pressurized to 30 bar by introducing 99.9% pure CO₂ gas into the solid suspension until hydrate formed. The CO₂ gas was constantly supplied into the vessel to maintain the working pressure. The running time for the hydrate formation period was measured from the introduction of CO₂ gas until the sharp temperature change is observed. The sudden temperature change is accompanied by the observation of thin-layered CO₂ hydrate (<1 mm) at the gas-water interface. The CO₂ hydrate was allowed to fully develop in the reaction vessel. The hydrate formation was monitored visually through the sight ports. The pressure in the vessel was also monitored during the hydrate formation period. The hydrate formation experiments were continuously carried out using different types of solids and electrolytes. Two isothermal conditions, 273.4 and 277.1 K, were employed to determine the effect of temperature on hydrate formation and followed the same procedures as described above. Control tests using 99.999% air were performed in

the solid suspensions by following the experimental steps above.

In order to calculate the amount of gas uptake during hydrate formation at different solid suspensions, a slightly different experimental procedure was followed. The slight modification was the control of CO₂ gas into the vessel. The

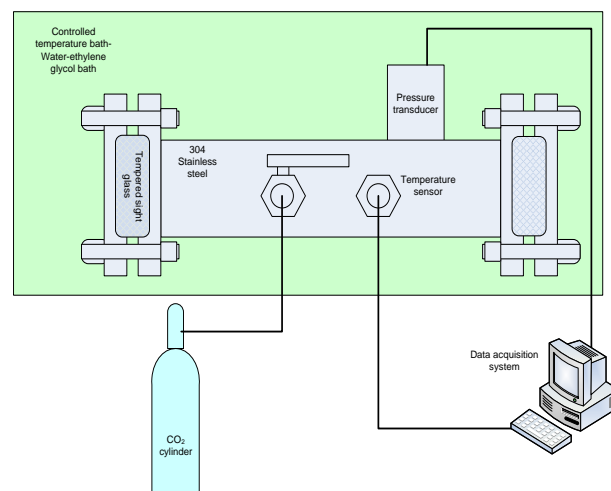


Figure 1 Schematic diagram of experimental set-up

vessel was pressurized to 30 bar by introducing 99.9% pure CO₂ gas into the solid suspension and was maintained within 20 minutes. After 20 minutes, the valve was closed. The experiment continued until no pressure changes have been monitored after hydrate formation. Typical pressure readings are shown in Figure 2a and 2b. Hydrate formation times were determined by monitoring the sharp increase in temperature, as shown in Figure 3. When the structures fall into crystalline arrangements, the samples give off heat or the latent heat is released and the temperature readings increases suddenly, showing a clear peak signal. T_s and T_p, are noted as start of temperature and peak temperature, respectively.

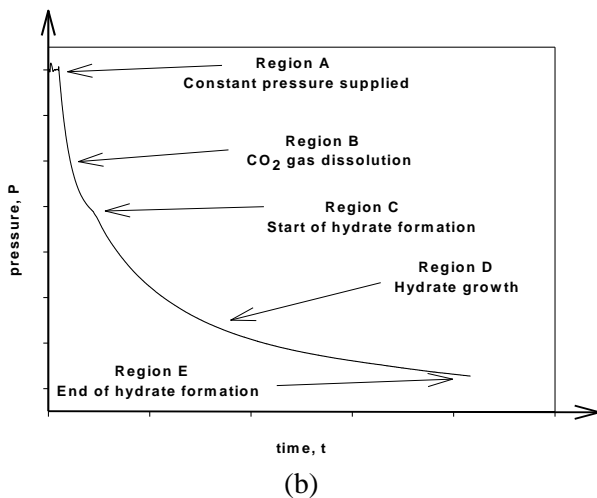
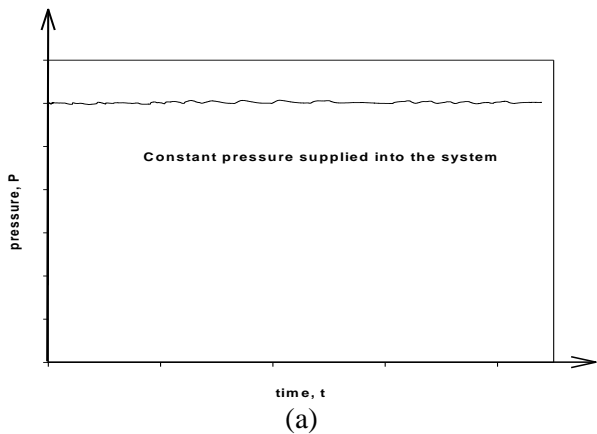


Figure 2 Pressure plot over time. a) The system pressure observed in monitoring the hydrate formation time. b) The gas uptake curve observed during hydrate formation and growth.

RESULTS AND DISCUSSION

Temperature changes during hydrate formation

Gas hydrate formations are considered as crystallization processes due to its ice-like structure. The process undergoes a phase change from a disordered gas and liquid water molecules to an ordered solid. An induction period is needed for the host (water) and guest (gas) molecules to rearrange into the orderly hydrate crystal structure. Heat is released as a result of phase change during crystallization. Release of latent heat during hydrate formation can cause an increase in temperature. Figure 2 shows the sharp increases in temperature that were all observed in solid suspensions and simultaneously observing the hydrate formation through the tempered sight

glasses. Temperature readings observed ranged from 0.2-2.0°C values. Hydrates formed at quiescent conditions. The decrease in temperature after it reached the peak temperature, T_p , indicates the latent heat was carried away by thermal conduction along the hydrate surroundings. No effort was done to measure the heat flow or heat dissipation along the hydrate layer. Studies on this heat dissipation as well as the thermal properties of the resulting hydrates are underway. Ice was not observed without CO₂ injection at the same experimental condition. Crystal hydrate was not observed when air (99.999% purity) was injected at the same experimental conditions. These two observations served as control tests and are shown in Figure 3. Slight changes of $\pm 0.2^\circ\text{C}$ in the graph were due to the bath temperature fluctuations or the injected gas temperature.

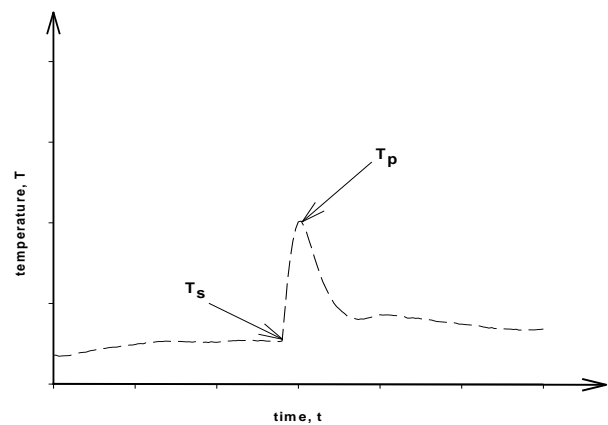


Figure 3 Temperature plotted over time. The start of hydrate formation is detected by a sharp increase in temperature. Start of temperature, T_s , and peak temperature, T_p , are indicated.

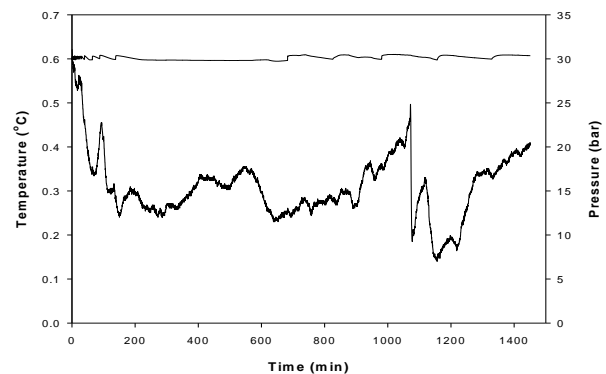


Figure 4 Control tests showed no clear increase in temperatures indicating no hydrate formation.

Hydrate formation at different solid suspensions

Carbon dioxide hydrate formations in solid suspensions in aqueous non-electrolyte and electrolyte solutions were monitored. The bath temperature was set to 273.4 K however, some measurement readings showed about 273.6-273.7 K values. These changes were due to the bath temperature fluctuations or the injected gas temperature. The initial temperature increase was due to gas injection into the vessel reactor.

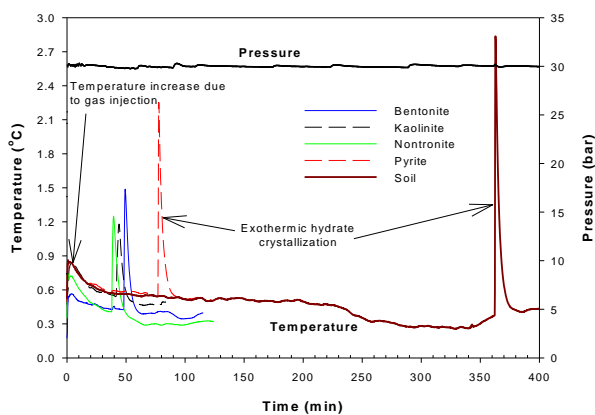


Figure 5 Distinct temperature peaks as hydrate formation were observed to form in solid suspensions without electrolytes at system conditions of 30 bar and 273.4 K.

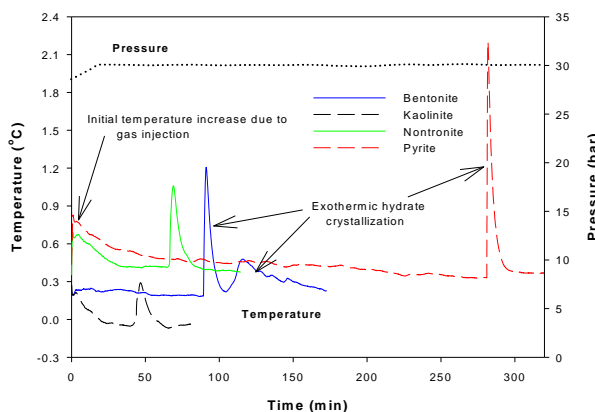


Figure 6 Distinct temperature peaks as hydrate formation were observed to form in solid suspensions containing 3.5% NaCl at system conditions of 30 bar and 273.4 K.

The results showed in Figure 5 that hydrate formation times for clay minerals in water were approximately twice and 10 times faster than that for pyrite and soil, respectively. The general trend observed from the results was the faster hydrate formations occurring in solid suspensions without electrolytes compared in solid solutions with electrolytes. Figure 6 showed slower hydrate formations in 3.5% NaCl suspensions. This may be due to the competition between the hydrate-forming molecules and dissolved ions for the hydrate formation sites on the solid surfaces. Studies have shown that electrolyte ion hydration competes with the availability of water molecules for the gas hydrate formation [9-10]. This competition affects the amount of time for the gas and water molecules to rearrange into the ordered crystalline structure.

Hydrate formations in clay suspensions were generally observed to form earlier than in pyrite and soil suspensions. The differences of the hydrate formation times in different solid suspensions and in different aqueous electrolyte suspensions at controlled temperature and pressure conditions additionally suggest other formation mechanisms. Although, several papers have suggested that hydrate formation is a stochastic behavior, we will use the hydrate formation time to evaluate the gas-solid-water interactions during hydrate formation processes [11-12]. Chemical interactions or chemical affinities between solid surfaces, gas and water molecules might be involved in the hydrate lattice structure rearrangement before triggering the start of hydrate crystallization.

Pyrite is an interesting solid surface due to its simple chemical formula and structure compared to the other solid surfaces used in this experiment. We can infer that the CO_2 gas and water molecules have a certain affinity to the clays and soil surfaces due to the layered or stacked molecular arrangements and easily served as hydrate lattice templates. Molecular simulations have shown that a methane hydrate interlayer complex has formed in smectite clays. This interlayer complex served as a nucleation site [13-14]. We can infer that CO_2 gas molecules behave similarly into the stacking layers of the clays. In one molecular simulation study, the authors showed that on a planar pyrite surface structure, the water molecules were found to absorb flat onto the surface, the oxygen atoms

bonded to a surface iron atom while the 2 hydrogens coordinate to surface sulfur atoms [15]. The network of interactions among between the sulfur and iron atoms and water molecules may contribute to a slower hydrate formation in the pyrite suspensions compared with the clay suspensions. No hydrate formation study has been conducted with pyrite however they have been implicated as possible geochemical indicators in the exploration of marine gas hydrates.

The formation of hydrates in the soil suspension proved to be a complicated among the solid suspensions. An earlier study conducted in a slight different experimental procedure has shown the earliest hydrate formation time in solid suspensions without electrolytes. However, in the current study, the hydrate formed last among the solid suspensions, almost five times late compared in the other suspensions. Additional studies are underway in order to understand this phenomenon.

Hydrate formation at two reactor temperatures (273.4 K and 277.1 K)

Figure 7 shows the hydrate formation times in the clay suspensions at two different bath temperatures (273.4 K and 277.1 K). It is observed that a higher temperature of 277.1 K generally affected the hydrate formation time into slightly slower hydrate formation times compared at 273.4 K. At 273.4, hydrate formed first in the kaolinite suspension followed by nontronite and bentonite. The same order of the formation time was observed at 277.1 K. These differences were reasonably anticipated since it is easier to form crystalline structures at lower temperatures. It shows that the temperature variable is an important parameter in hydrate formation processes. No chemical interactions were expected to be associated at these experimental conditions.

CO₂ gas uptake during hydrate formation at different solid suspensions

As explained in the experimental procedure above, a slightly different step was followed for the monitoring of the CO₂ gas uptake. As shown in Figure 2, there are four regions observed during these experimental conditions. Region A showed the constant supply of CO₂ into the vessel for 20

minutes. Region B was the period of CO₂ dissolution, while Region C was the start of hydrate formation, where a sudden slope change was observed. There was no significant change in the pressure readings at Region D which indicated the end of hydrate formation.

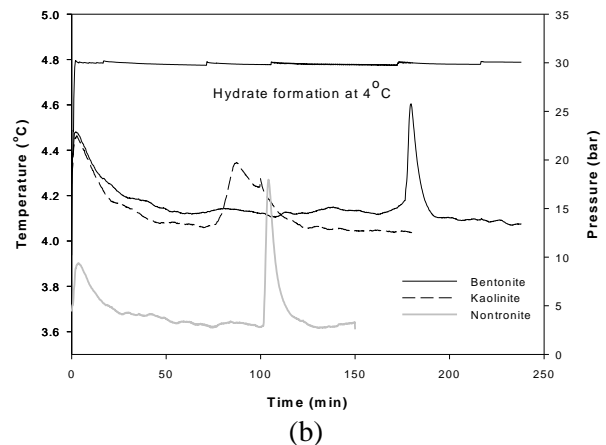
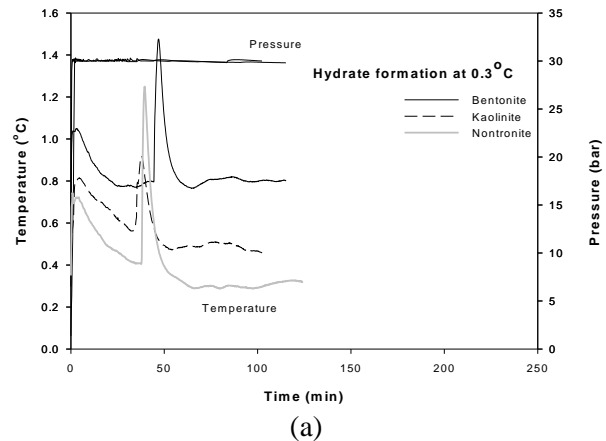


Figure 7 Hydrate formation at bath temperatures (a) 273.4 K and (b) 277.1 K.

There were peculiar observations during these experimental conditions. The encircled region at Figure 8 showed two slope changes in approximately 40 minutes. At this period we moreover visually monitored a rapid mass hydrate formation. The slope seemed a linear slope and we decided to measure this time range as the rate of gas consumption. The pressure axis was converted to moles before linearization. The amount of moles consumed during hydrate formation was done using:

$$n = PV/zRT \quad (3)$$

where the variables are pressure, P, temperature, T, compressibility factor, z, gas constant ($8.314 \text{ m}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), and volume, V. Based on our results, the kaolinite appeared to have the fastest gas consumption rate among the clay mineral suspensions, which was 2.4 times and 7.4 times faster than nontronite and bentonite, respectively. We have monitored this condition at non-electrolyte suspensions only.

However, we have also monitored the average consumption rate during hydrate formation, that is, from Region C to Region D. The average consumption rate (r) was calculated using:

$$r = \frac{P_s - P_e}{t_e - t_s} \quad (4)$$

where P and t were pressure and time variables, respectively. We got different results and in the order of kaolinite, bentonite, and nontronite. Kaolinite has a gas consumption rate of 1.7 times faster than bentonite and 1.1 times faster than nontronite. The possible reason in these differences was the input value of length of the hydrate formation period compared to the earlier calculations. Secondly, the mass of hydrates must have clogged the connection where the pressure transducer was located and affected the measurement readings. We believed that the first calculation was the reliable gas consumption rate calculation than the second one.

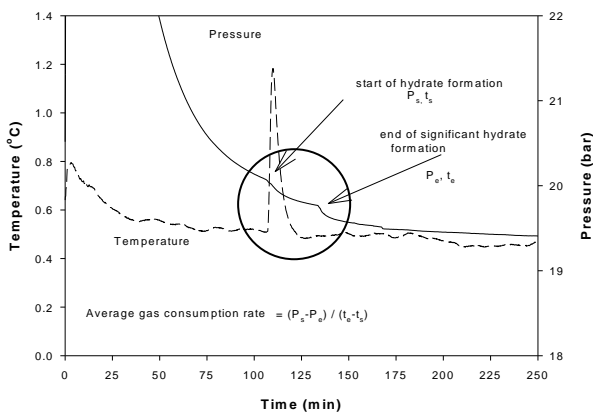
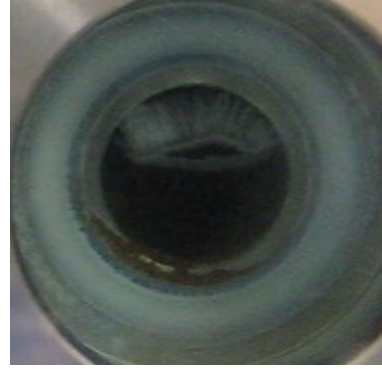
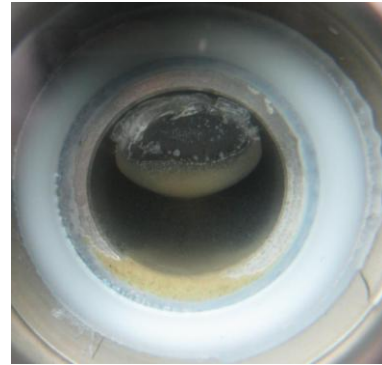


Figure 8 Observed slope change during hydrate formation in bentonite-in-water suspension.



(a)



(b)

Figure 9 Visual observation of hydrate formation in solid suspensions prepared in a) deionized water and b) 3.5% NaCl.

Figure 9 and 8b shows hydrate formation in non-electrolyte solution and 3.5% NaCl solution, respectively. We visually observed that larger mass of hydrates formed in non-electrolyte solutions than in electrolyte solutions. We determined the CO_2 gas uptake during hydrate formation using pressure monitoring to verify these observations. Based on our calculations, it was observed that the hydrate formed in 3.5% NaCl showed a higher gas uptake compared with the non-electrolyte suspension. These comparisons were illustrated in Figures 10 and 11. The possible reason must be the mass of hydrates have clogged the connection where the pressure transducer was located and affected the measurement readings. The dissociation of the carbon dioxide hydrate might have offered additional information on this gas uptake, however, no effort was conducted to measure the gas release during hydrate dissociation.

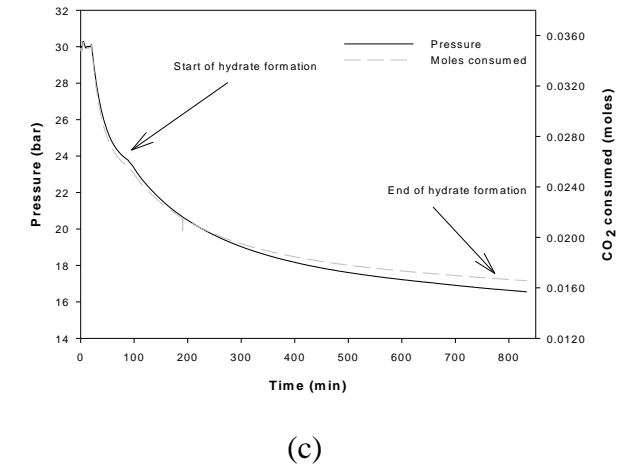
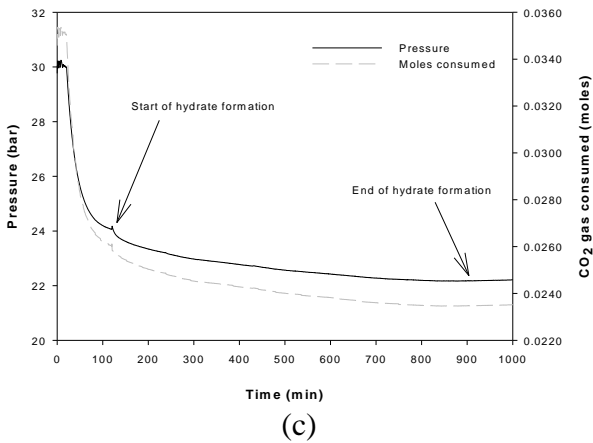
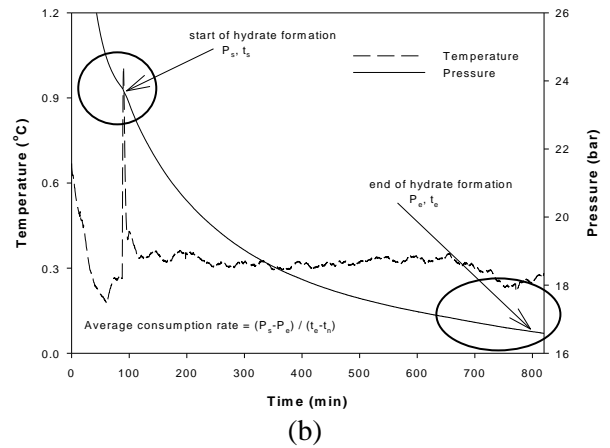
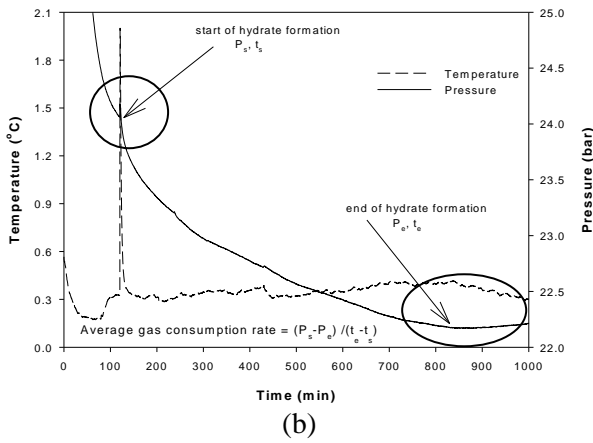
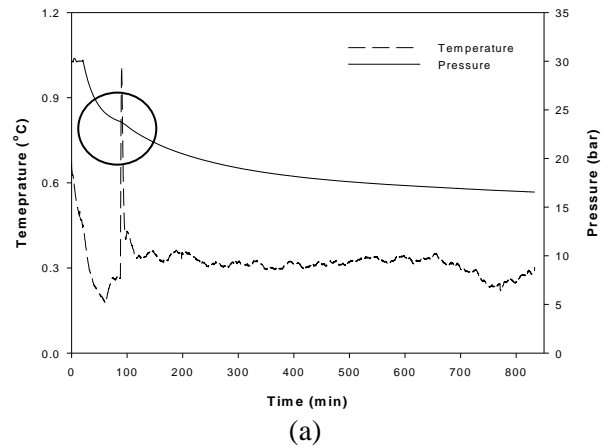
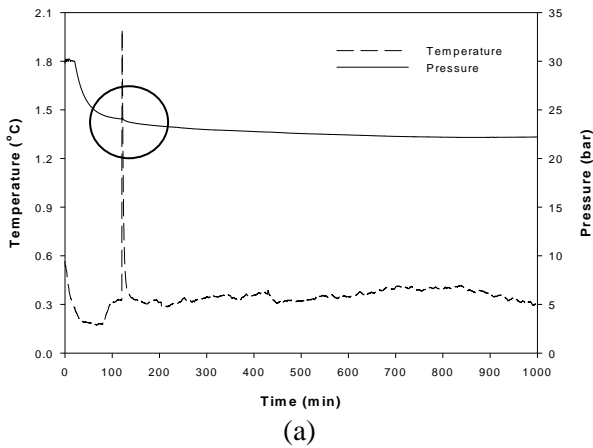


Figure 10 Hydrate formation in soil non-electrolyte suspension at (a) normal temperature and pressure monitoring of the system (b) magnified region of hydrate formation (c) gas consumption curve

Figure 11 Hydrate formation in soil 3.5 % NaCl suspension at (a) normal temperature and pressure monitoring of the system (b) magnified region of hydrate formation (c) gas consumption curve

Conclusions

In this work, we have evaluated the effects of different solid suspensions in different electrolytes on the hydrate formation time. We additionally showed the effect of solid suspensions and solid suspensions in electrolytes on gas uptake or gas consumption rate. Results from these experiments will be helpful in providing an insight on the formation and growth of carbon dioxide hydrate, once sequestered into the geological formations.

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