

# Influence of Sand Particle Size on the Kinetics of CO<sub>2</sub> Hydrate Formation in a Pilot Scale Reactor

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## ABSTRACT

CO<sub>2</sub> storage in the reservoir is the most common method to mitigate global warming. In this work, the influence of sand particle size on the CO<sub>2</sub> hydrate formation kinetics has been investigated in a pilot-scale reactor (25 L) at three different sand particle sizes (300-500 μm, 500-710 μm, and 710-1000 μm). The experiments are carried out at 275.15 K temperature and initial pressure of 3.5 MPa. The parameter studied in the present work are induction time, amount of gas consumption during hydrate formation, water to hydrate conversion, and hydrate saturation. It is observed that the induction time is lowest for the smaller sand particle size. Gas consumption, water to hydrate conversion, and hydrate saturation are higher for smaller sand particle sizes. The results show that smaller sand particle size enhances the hydrate formation kinetics. The present study can be helpful in selecting a suitable reservoir for CO<sub>2</sub> sequestration via hydrate formation.

**Keywords:** Sand particles, Porous media, Gas hydrate, Induction time, Hydrate formation

## 1. INTRODUCTION

Global warming has become an international problem in the present day due to the increase of CO<sub>2</sub> in the atmosphere. Fossil fuel-based power plants are the primary source of CO<sub>2</sub> emissions, accounting for one-third of global CO<sub>2</sub> emissions. Therefore, it is very important to capture and safely store CO<sub>2</sub> to reduce the effect of global warming. The CO<sub>2</sub> capture and sequestration (CCS) technique is the most promising way to mitigate global warming. In oil production sites, CO<sub>2</sub> gas is injected to enhance the oil recovery by replacing oil with CO<sub>2</sub> molecules, and CO<sub>2</sub> gas is stored in the pore

space of the reservoir. The disadvantage associated with this method is that the stored CO<sub>2</sub> may be leak from the injection site and alter the aquatic life. There are several advantages of CO<sub>2</sub> storage via hydrate formation [1]. It reduces the chance of leakage of CO<sub>2</sub> from injection sites and simultaneous production of methane gas from methane hydrate [2]. Gas hydrates are crystalline compounds in which hydrogen-bonded water molecules encage gas molecules at suitable thermodynamic conditions [3]. Gas hydrates are mainly found in deep-sea and permafrost regions [4]. There are several industrial applications of gas hydrates such as CO<sub>2</sub> captures [5], seawater desalination [6], gas separation [7], and natural gas storage and transportation [8], etc.

In recent years, CO<sub>2</sub> storage via hydrate formation attained much popularity in the scientific community due to safe and efficient techniques. A large amount of CO<sub>2</sub> gas can be stored in the form of CO<sub>2</sub> hydrate. The storage of CO<sub>2</sub> gas in the reservoir through the hydrate formation depends on several factors such as pressure, temperature, permeability, porosity, and reservoir salinity [9], etc.

In the present study, three different sand particle sizes are used to evaluate the influence of particles size on the hydrate formation kinetics. Further, induction time, gas consumption, water to hydrate conversion, and hydrate saturation are studied for different sand particle sizes.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials

Indian standard sand is used as a porous media with three different particle sizes from 300-500 μm, 500-710 μm, and 710-1000 μm and procured from Tamil Nadu

Selection and peer-review under responsibility of the scientific committee of the 13<sup>th</sup> Int. Conf. on Applied Energy (ICAE2021).

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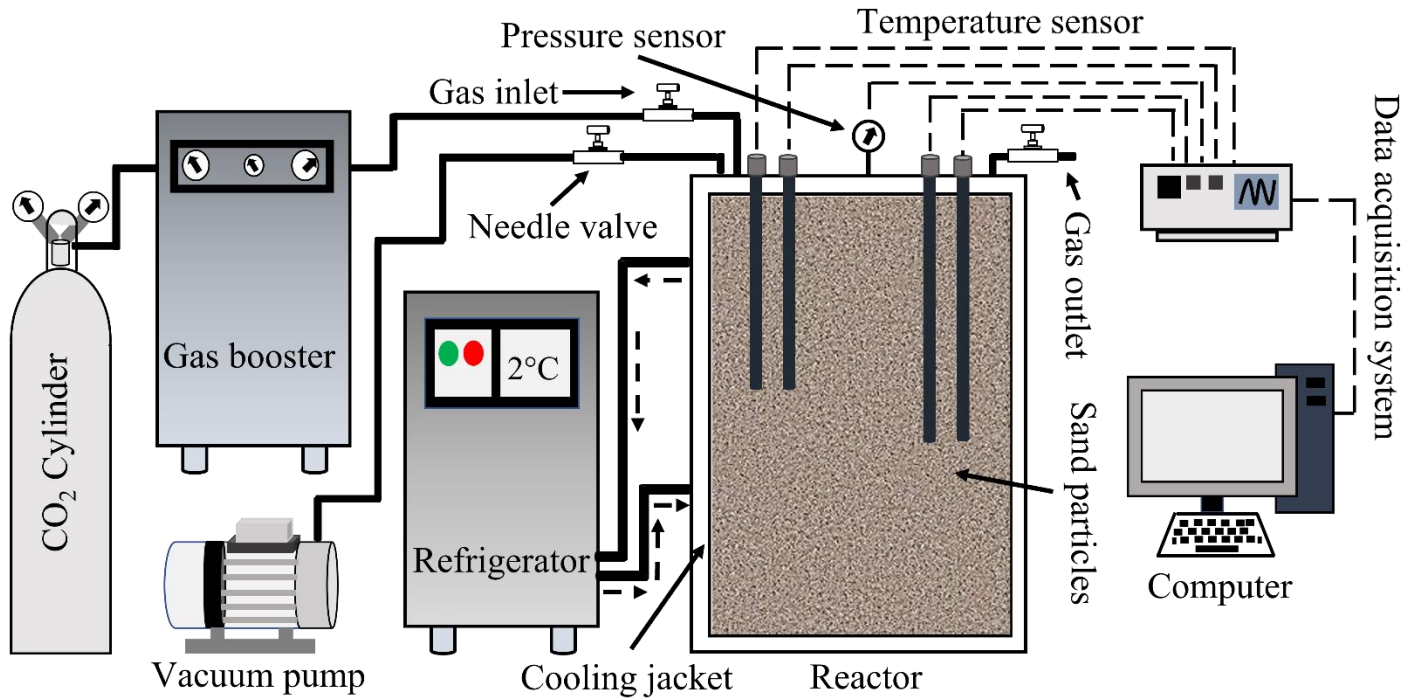


Fig. 1. Schematic diagram of the experimental setup

Minerals limited India. Table 1 provides the details of sand particles. CO<sub>2</sub> gas with 99.9% purity is purchased from Sigma gases and services India, and deionized water (DI) is taken from special water facility IIT Kanpur India. Table 1. Properties of the sand particle.

Sand particle size ( $\mu\text{m}$ )	Porosity (%)	Bulk density ( $\text{kg}/\text{m}^3$ )
300-500	38.64	1.62
500-710	39.77	1.59
710-1000	40.15	1.58

## 2.2 Experimental setup and experimental procedure

The schematic diagram of the experimental setup is shown in Fig. 1. The internal diameter and height of the 25 liters high-pressure reactor are 232 mm and 622 mm, respectively. The reactor is made of stainless steel (SS-316) with designed pressure of 18 MPa. A cooling jacket surrounds the reactor, and the cooling jacket is connected to the refrigerator to maintain the required temperature around the reactor wall. The reactor is installed with four RTD sensors, measuring accuracy of  $\pm 0.1^\circ\text{C}$ . These RTD sensors are placed in two pairs. The first pair is 313 mm in height, and the second pair is 326 mm in height. The RTD is located at 69 mm and 100 mm, respectively, from the reactor center. A pressure sensor (Model: Wika A-10) measuring accuracy of  $\pm 0.1$  bar and a pressure gauge are mounted at the reactor head to

measure the gas pressure. Gas supplied from the CO<sub>2</sub> cylinder is boosted using a booster pump to the desired pressure to deliver in the reactor. The experimental data is recorded by a data acquisition system with the help of LabView software and stored in a personal computer (PC).

The reactor is washed with deionized water. Subsequently, preparation of the sand bed is done using the layer-wise pattern. The reactor is filled with sand in layer-wise to avoid the formation of air pockets in the reactor. The layers are constructed by filling 2025 gm of sand at once, followed by adding the corresponding amount of DI water required for 50% sand saturation. The process is repeated 20 times to fill the reactor completely. A total amount of 40.5 Kg of sand and 4.83 L of DI water is utilized for 300-500  $\mu\text{m}$  sand size. Table 2 provides the detail for sand particles, and DI water are required to completely fill the reactor in case of 500-710  $\mu\text{m}$  and 710-1000  $\mu\text{m}$  sand particles. The reactor is then closed and airtight with the reactor head. A vacuum pump is used to develop a vacuum pressure of 1kPa inside the reactor. The reactor is subsequently cooled to the desired experimental temperature of 275.15 K. The reactor is purged three times with CO<sub>2</sub> gas to remove air from the reactor and establish only CO<sub>2</sub> environment. Finally, the CO<sub>2</sub> gas is charged in the reactor at the experimental pressure of 3.5 MPa. The hydrate nucleation is marked by a sudden spike in temperature

and a decrease in pressure profile. The CO<sub>2</sub> gas pressure continuously decreases during the hydrate formation process. The experiment is completed when the pressure profile is stable for more than 2 hours. The data acquisition system is activated to record the temperature and pressure information and store it in the personal computer at 20 sec intervals.

Table 2. Details of amount sand particles and DI required for different sizes of sand particles.

Sand particle size (μm)	Sand mass (Kg)	DI water(L)
300-500	40.5	4.83
500-710	39.75	4.97
710-1000	39.50	5.02

### 2.3 Calculation procedure

The following section calculates the amount of gas consumption during hydrate formation, water to hydrate conversion, and hydrate saturation.

The amount of gas consumption is calculated by the following equation.

$$\Delta n_{CO_2} = n_0 - n_t = \frac{P_0 V_0}{z_0 R T_0} - \frac{P_t V_t}{z_t R T_t} \quad (1)$$

Where  $n$ ,  $P$ ,  $V$ ,  $z$ ,  $R$ , and  $T$  are moles of CO<sub>2</sub> gas, gas pressure, gas volume, compressibility factor, gas constant, and reactor temperature, at time  $t = 0$  and time  $t = t$ , respectively. Pitzer's correlation is used for the calculation of the compressibility factor.

$$z_t = 1 + \left[ 0.083 - 0.422 * \left( \frac{T_c}{T_t} \right)^{1.6} \right] \frac{P_t T_c}{P_c T_t} + \omega \left[ 0.139 - 0.172 * \left( \frac{T_c}{T_t} \right)^{4.2} \right] \frac{P_t T_c}{P_c T_t} \quad (2)$$

Where  $T_c$ ,  $P_c$ , and  $\omega$  represents critical temperature, critical pressure, acentric factor, and their value are 304.2K, 7.338 MPa, and 0.224, respectively.

Water to hydrate conversion is defined as the ratio of water moles engaged in the hydrate formation to initial water moles. The following formula is used for the calculation:

*Water to hydrate conversion (%)*

$$R_w = \frac{M \times \Delta n_{CO_2}}{n_{w_0}} \times 100 \quad (3)$$

where  $M$ ,  $\Delta n_{CO_2}$ , and  $n_{w_0}$  denote the hydration number, gas consumed, and initial water moles, respectively.

Hydrate saturation is calculated by using the following equation.

$$\text{Hydrate saturation } S_h = R_w \times S_w \times 1.1 \quad (4)$$

where  $S_w$  is the initial water saturation of the sand particles. The water volume is expanded after converting into hydrate and can be assumed 1.1 times the initial water.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of sand particle size on induction time

Fig. 2 shows the induction time of CO<sub>2</sub> hydrate formation for three different sand particle sizes. The induction time is defined in the present work as the time at which a sudden increase in the temperature profile and decrease in pressure profile due to hydrate formation from the start of the experiment. The increase in the temperature profile is due to the exothermic nature of the hydrate formation process. The decrement in the pressure is because of entrapped gas in the hydrogen-bonded cage structure. The induction time involves the formation of stable nuclei for hydrate formation. Fig. 2 shows that the induction time increases with the increase in the size of sand particles. The induction time for the sand particle size 300-500 μm, 500-710 μm, and 710-1000 μm are 52.5 hr, 57.3 hr, and 66.8 hr, respectively. The variation of induction time for different sand particles size is due to the porosity and pore space of sand particles changing with the different sizes of sand particles, leading to the different hydrate nucleation environments [10]. Gas hydrates are primarily formed in the pore space of the sand particles.

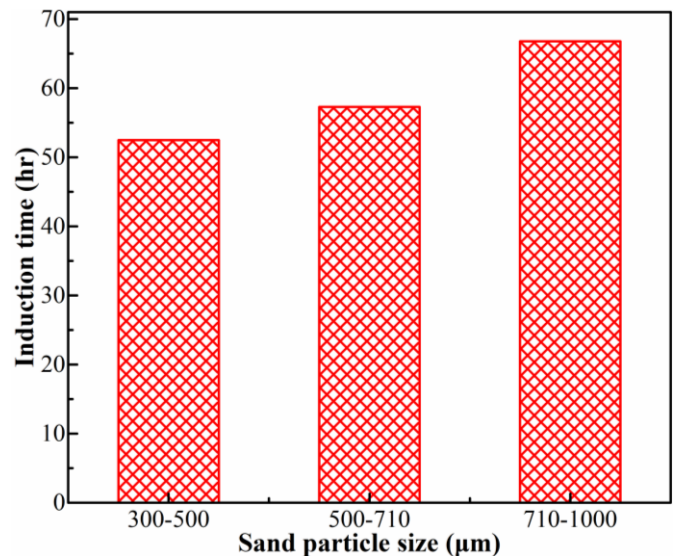


Fig. 2. Induction time of CO<sub>2</sub> hydrate formation for different sand particle size

### 3.2 Effect of sand particle size on gas consumption

Fig. 3 shows the amount of gas consumption during the hydrate formation process for different sand particle sizes. The amount of gas consumption during the hydrate formation process is calculated by Eq. 1. It is found that the gas consumption continuously increases during the hydrate formation process. The gas consumption rate is higher at the initial stage of the hydrate formation process, and it decreases with time during the hydrate formation process. The above phenomena are due to the CO<sub>2</sub> hydrate formed in the pore space of the sand particles, and it resists the movement of CO<sub>2</sub> gas molecules in the pore space of sand particles. Gas consumption for the sand particle size 300-500 μm, 500-710 μm, and 710-1000 μm are 5.46 mol, 5.01 mol, and 4.63 mol, respectively. The result shows that the gas consumption increases with a decrease in the sand particle size. Smaller particle size provides more nucleation sites for the hydrate formation and larger specific surface area contact between water and gas molecules than larger particle size. Therefore, more nucleation sites enhance the hydrate formation kinetics and increase the total gas consumption during the hydrate formation process.

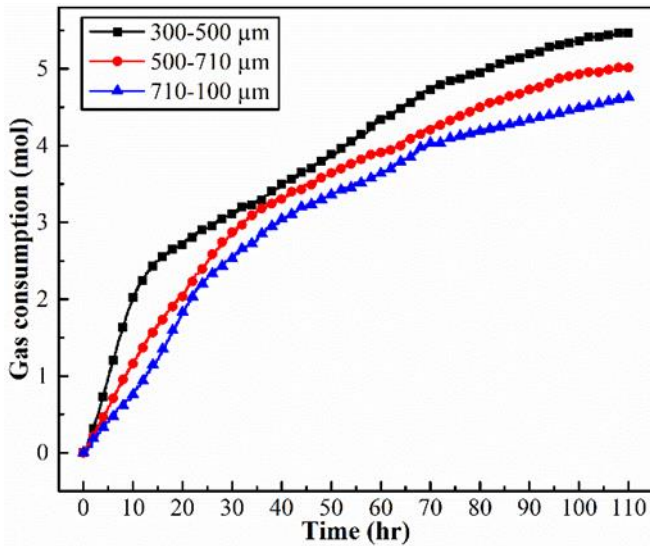


Fig. 3. Amount of gas consumed during CO<sub>2</sub> hydrate formation for different sand particle size

### 3.3 Effect of sand particle size on the water to hydrate conversion and hydrate saturation

Fig. 4 shows the water to hydrate conversion and hydrate saturation at the completion of the hydrate formation process for different sand particle sizes. Water to hydrate conversion value and hydrate saturation are calculated by using Eq. 3 and Eq. 4, respectively. The

water to hydrate conversion values for the sand particle size 300-500 μm, 500-710 μm, and 710-1000 μm are 12.8%, 11.41%, and 10.43%, respectively. Water to hydrate conversion value decreases with an increase in the size of the sand particle, and the maximum value is achieved for 300-500 μm sand particle.

Hydrate saturation for the sand particle size 300-500 μm, 500-710 μm, and 710-1000 μm are 7.04 %, 6.27 %, and 5.74 %, respectively. Results show that the hydrate saturation depends on the sand particles size, and maximum hydrate saturation is found for the smaller sand particle size.

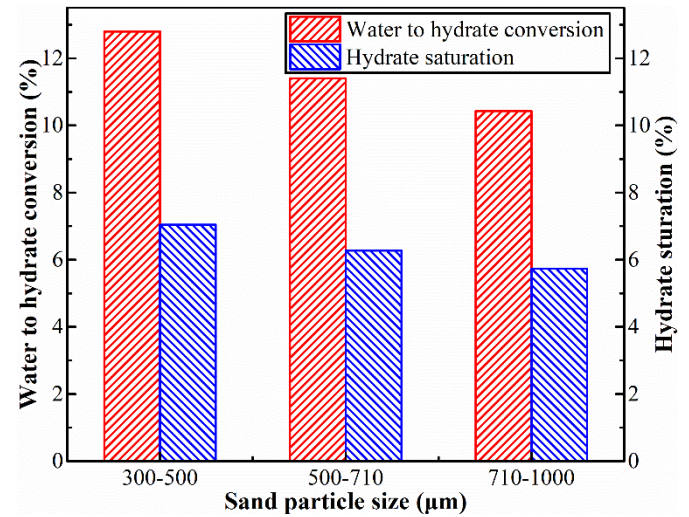


Fig. 4. Water to hydrate conversion and hydrate saturation for different sand particle size

Fig. 5 shows the CO<sub>2</sub> hydrate formation in the pore space of sand particles at several locations. Initially, loose sand particles are filled with 50% initial water saturation in the reactor. The hydrate formation process consolidates the porous media (sand particles) from its initial state. It is observed that the hydrate formation in

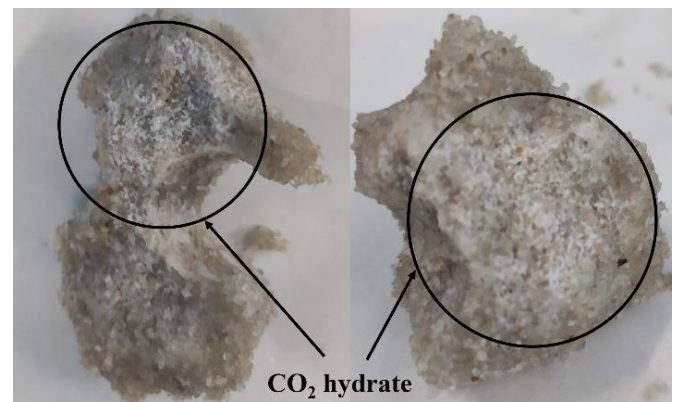


Fig. 5. CO<sub>2</sub> hydrate formed in the pore space of sand particles



porous media is spatially inhomogeneous, and the whitish colour can identify it in porous media. The black circle denotes the highly hydrate saturated region in the porous media.

#### 4. CONCLUSION

In this work, three different sand particles are used to study the CO<sub>2</sub> hydrate formation process. The influence of particle size on hydrate formation kinetics is investigated. It is observed the smaller sand particle shorten the induction time and enhance the hydrate formation kinetics. Induction time, amount of gas consumption, water to hydrate conversion, and hydrate saturation are 52.5 hr, 5.46 mol, 12.8%, and 7.04%, respectively, for 300-500 μm sand particles. Smaller sand particle provides a more specific surface contact area between water and gas molecules for hydrate nucleation than larger sand particle size. CO<sub>2</sub> hydrate formation in the pilot scale reactor provides important insights for mimicking the CO<sub>2</sub> sequestration via hydrate formation at the field scale.

#### ACKNOWLEDGEMENTS

We greatly acknowledge the support provided by IIT Kanpur for the present work.

#### REFERENCE

- [1] Zheng J, Chong ZR, Qureshi MF, Linga P. Carbon Dioxide Sequestration via Gas Hydrates: A Potential Pathway toward Decarbonization. *Energy and Fuels* 2020;34:10529–46. <https://doi.org/10.1021/acs.energyfuels.0c02309>.
- [2] Chen Y, Gao Y, Zhao Y, Chen L, Dong C, Sun B. Experimental investigation of different factors influencing the replacement efficiency of CO<sub>2</sub> for methane hydrate. *Appl Energy* 2018;228:309–16. <https://doi.org/10.1016/j.apenergy.2018.05.126>.
- [3] Englezos P. Clathrate Hydrates. *Ind Eng Chem Res* 1993;32:1251–74. <https://doi.org/10.1021/ie00019a001>.
- [4] Sloan ED, Koh CA. Clathrate hydrates of natural gases, third edition. 2007.
- [5] Ansari AA, Ravesh R, Das MK, Panigrahi PK. Carbon dioxide hydrate formation in porous media, 2020. <https://doi.org/10.1615/ihmtc-2019.360>.
- [6] Lv Q, Li X, Li G. Seawater desalination by hydrate formation and pellet production process. *Energy Procedia* 2019;158:5144–8. <https://doi.org/10.1016/j.egypro.2019.01.684>.
- [7] Eslamimanesh A, Mohammadi AH, Richon D, Naidoo P, Ramjugernath D. Application of gas hydrate formation in separation processes: A review of experimental studies. *J Chem Thermodyn* 2012;46:62–71. <https://doi.org/10.1016/j.jct.2011.10.006>.
- [8] Veluswamy HP, Wong AJH, Babu P, Kumar R, Kulprathipanja S, Rangsunvigit P, et al. Rapid methane hydrate formation to develop a cost effective large scale energy storage system. *Chem Eng J* 2016;290:161–73. <https://doi.org/10.1016/j.cej.2016.01.026>.
- [9] Sun D, Ripmeester J, Englezos P. Phase Equilibria for the CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub>/H<sub>2</sub>O System in the Hydrate Region under Conditions Relevant to Storage of CO<sub>2</sub> in Depleted Natural Gas Reservoirs. *J Chem Eng Data* 2016;61:4061–7. <https://doi.org/10.1021/acs.jced.6b00547>.
- [10] Liu Z, Pan Z, Zhang Z, Liu P, Shang L, Li B. Effect of Porous Media and Sodium Dodecyl Sulphate Complex System on Methane Hydrate Formation. *Energy and Fuels* 2018;32:5736–49. <https://doi.org/10.1021/acs.energyfuels.8b00041>.