Desalination and Water Treatment
www.deswater.com

28 (2011) 59–64
April

1944-3994/1944-3986 © 2011 Desalination Publications. All rights reserved
doi: 10/5004/dwt.2011.2201

Simultaneous water desalination and CO_2 capturing by hydrate formation

Mohammad Sarshar*, Abdul Hussein Sharafi

Fars Engineering Research Center, Engineering Research Institute, Janbazan Avenue, Modaress Bulverde, Shiraz, Iran
Tel. +98 711 7218113; email: sarshar@shirazu.ac.ir

Received 1 March 2009; Accepted 1 July 2010

ABSTRACT

Stabilizing CO_2 concentration in the atmosphere is vital because of the increasing rate of using fossil fuels in the industries and buildings for heating purposes. Further, shortage of potable water in most of the world needs cheap and efficient methods for desalination of seawater. CO_2 hydrate is a good solution for both problems. By CO_2 hydrate formation in the presence of seawater, CO_2 is captured and stored in a safe place. Then it is decomposed to carbon dioxide and desalinated water where they are desired. Afterward, desalinated water is consumed by any leaving thing and CO_2 is consumed by plants. In this study, CO_2 hydrate is formed at 2.5–4.5 MPa and 0–8 °C in a 5 l semi-batch reactor in the presence of synthetic saline waters and Persian Gulf water. In all experiments, two stages of CO_2 dissolution and hydrate formation are observed. After ending hydrate formation, pressure is released and temperature is gradually increased to take effect the decomposition. The salinity of the produced water is measured and compared to raw water salinity to define the efficiency of the separation. The separation efficiencies of the dissolved solids are measured about 6–52% in most of the experiments.

Keywords: Batch reactor; Capture; CO_2 hydrate; Kinetics; Sequestration

1. Introduction

Reducing the concentration and storing CO_2 away from the atmosphere is a challenging subject for the scientists. CO_2 storage in the form of hydrate on the ocean's bed is one of the new methods for the CO_2 sequestration [1].

CO_2 hydrates (CO_2, 5.75–6.00 H_2O) are crystalline solids that are more properly called clathrate hydrates to distinguish them from stoichiometric hydrates found in inorganic chemistry [2].

Sarshar and Fathikalajahi [3] studied the kinetics of CO_2 hydrate formation in saline waters in a 3 l semi-batch reactor at 3.0–4.4 MPa and 0–5 °C. They distinguished three stages of hydrate formation such as CO_2 dissolution, nucleation and growth by measuring CO_2 consumption versus time.

Lee et al. [4] produced gas hydrate from CO_2/H_2 gas mixtures with the addition of tetrahydrofuran (THF) in a semi-batch stirred vessel at various pressures and temperatures to investigate the CO_2 separation and recovery properties. They determined the gas uptake during hydrate formation and composition changes in the gas phase by gas chromatography. They observed the impact of THF on hydrate formation from the CO_2/H_2. They found 1.0 mol% of THF to be the optimum concentration for CO_2 capture based on kinetic experiments.

Kumar et al. [5] developed a hybrid process for the capture of CO_2 and H_2 from a treated fuel gas mixture. Their process consisted of two hydrate crystallization stages operating at 273.7 K and 3.8 and 3.5 MPa, respectively. These operating pressures at the crystallization stages were possible by adding 2.5% by mole propane. Propane enabled the reduction in the hydrate formation pressure and thus reduced the cost associated with

---

*Corresponding author.

Presented at the 1st International Conference on Water and Wastewater Treatment, April 21–22, 2010, Isfahan, Iran

the compression of the fuel gas. The two hydrate stages operated at 7.5 and 3.5 MPa without adding propane.

Sarshar et al. [6] carried out a set of experiments at 279 K and 3.5–5 MPa to determine the rate of CO_2 hydrate formation reaction in a tubular reactor. Further, they developed a model for the prediction of the rate of hydrate formation reaction based on the mass transfer, crystallization and thermodynamic concepts. The predicted hydrate formation rates were in good agreement with the experimental data at different operating conditions.

Ersland et al. [7] reported experimental results of CH_4–CO_2 exchange within sandstone pores and measurements of gas permeability during stages of hydrate growth in sandstone core plugs. The formation of methane hydrate in porous media was monitored and quantified with magnetic resonance imaging techniques (MRI). Hydrate growth pattern within the porous rock was discussed along with measurements of gas permeability at various hydrate saturations. Gas permeability was measured at steady state flow of methane through the hydrate-bearing core sample. Experiments on CO_2 injection in hydrate-bearing sediments was conducted in a similar fashion. By use of MRI and an experimental system designed for precise and stabile pressure and temperature controls flow of methane and CO_2 through the sandstone core proved to be possible for hydrate saturations exceeding 60%.

Szymcek et al. [8] developed a three-phase, pilot-scale continuous-jet hydrate reactor (CJHR) for the production of gas hydrates. The reactor received water and a hydrate-forming species to produce the solid gas hydrate. The CJHR had been tested for the production of CO_2 hydrate for the purpose of ocean carbon sequestration. Formation of CO_2 hydrate was investigated using various reactor/injector designs in a 72 l high-pressure vessel. They designed a novel injector to improve the dispersion of one reactant into the other and, thus, eliminated mass transfer barriers that negatively affected conversion. An increase in the production rate of two orders of magnitude was also achieved. The designed injectors were tested in both distilled and saline water. Hydrate production experiments were conducted at different CO_2 and water flow rates and for pressures and temperatures equivalent to intermediate ocean depths (1100–1700 m).

Tsouris et al. [9] illustrated the issues related to the scale-up of continues jet hydrate reactor (CJHR). Hydrate was formed using two CJHR geometries; the first sprayed water in CO_2, and the second sprayed CO_2 in water.

Duc et al. [10] studied CO_2 capture from a gas mixture by hydrate crystallization. They conducted separation experiments using TBAB as an additive, which makes the hydrate crystallization condition milder. Based on the experimental results, flow sheeting simulations were carried out to evaluate a realistic energetic costing and were compared with other classical technologies (membranes, amines, etc.). The investment and production cost of the gas capture system for different kinds of blast furnaces were also estimated.

Linga et al. [11] studied medium-pressure CO_2 capture process based on hydrate crystallization in the presence of tetrahydrofuran (THF). Relevant thermodynamic data at 0.5, 1.0, and 1.5 mol% THF were obtained and reported. In addition, the kinetics of hydrate formation from the CO_2/N_2/THF system as well as the CO_2 recovery and separation efficiency was also determined experimentally at 273.75 K. The compression costs are reduced due to lower formation pressure from 75% to 53% of the power produced for a typical 500 MW power plant.

Linga et al. [12] carried out a set of experiments of gas hydrate formation from CO_2/N_2 and CO_2/H_2 gas mixtures in a semi-batch stirred vessel at constant pressure and temperature of 273.7 K. During hydrate formation the gas uptake was determined and the composition changes in the gas phase were obtained by gas chromatography. The rate of hydrate growth from CO_2/H_2 mixtures was found to be the fastest. In both mixtures CO_2 was found to be preferentially incorporated into the hydrate phase.

The observed fractionation effect was desirable and provided the basis for CO_2 capture from flue gas or fuel gas mixtures. The separation from fuel gas was also a source of H_2. The impact of tetrahydrofuran (THF) on hydrate formation from the CO_2/N_2 mixture was also observed. THF was known to substantially reduce the equilibrium formation conditions enabling hydrate formation at much lower pressures. THF was found to reduce the induction time and the rate of hydrate growth.

Linga et al. [13] illustrated the concepts and provided basic thermodynamic and the kinetic data for the conceptual design of CO_2 capturing systems which are applicable to the post- and pre-combustion processes. In addition, they presented hybrid conceptual processes for pre- and post-combustion capture based on hydrate formation coupled with membrane separation.

Buanes et al. [14] developed a model which was a hybrid of cellular automata and Monte Carlo to study the growth of CO_2 hydrate from aqueous solutions. They showed that, depending on how large the driving forces were, the hydrate crystal grew as compact structure or as a highly branched structure. Furthermore, they showed that the diffusion of CO_2 in the solution was the main limiting factor, unless the solution had a large supersaturation. Temperature effects were shown only to be important at large supersaturations.

Goel [15] summarized the current knowledge on producing methane gas from hydrates while simultaneously sequestering carbon dioxide gas as hydrates, and discussed the challenges and issues in its implementation.

Kvamme et al. [16] applied the techniques of magnetic resonance imaging (MRI) as a tool to visualize the conversion of CH_4 hydrate within Bentheim sandstone matrix into the CO_2 hydrate. They simulated corresponding model systems using the phase field theory approach. Their theoretical studies indicated that the kinetic behaviour of the systems closely resembled that of CO_2 transport through an aqueous solution. They interpreted this to mean that the hydrate and the matrix mineral surfaces were separated by liquid-containing channels. These channels served as escape routes for released natural gas, as well as distribution channels for injected CO_2.

Kang and Lee [17] developed a hydrate-based gas separation (HBGS) process especially for recovering CO_2 from flue gas. Tetrahydrofuran (THF) chosen as a hydrate promoter in the temperature range of 272–295 K. They verified that the process recovered more than 99 mol% of CO_2 from the flue gas.

Sarshar and Bonyadi [18] studied the experimental apparatus for water desalination using gas hydrate formation. They performed the experiments in a tabular circulating flow reactor at 6 °C and 3.5–5.0 MPa.

Javanmardi and Moshfeghian [19] estimated the required energy for seawater desalination based on their proposed hydrate formation process. Further, they presented economic evaluation and cost estimation of produced potable water. They prepared a computer program to simulate the proposed process and to estimate the total capital investment, operation and maintenance costs and total production cost.

McCormack and Anderson [20] presented preliminary research, design, clathrate freeze desalination method and system. They estimated the cost for a clathrate former which was injected through the inner pipe of a submerged pipeline to a predetermined ocean depth at which the ocean temperature was less than the clathrate forming temperature. The agent combined with seawater within the annulus of the outer pipe to form slurry of clathrate ice crystals and brine that was pumped to the surface. The ice crystals were separated from the brine, washed, and melted; the remaining water was then separated from the clathrate forming agent and discarded. The system depicted used the hydrocarbon R141B (di chloro mono fluoro ethane – $CH_3 C1_2F$) as the clathrate forming agent with lesser attention on R22 (chloro di fluoro methane – $CHClF_2$) and carbon dioxide (CO_2).

In the present study, a semi-batch reactor is fabricated to study the simultaneous CO_2 capture and water desalination using saline and Persian Gulf Waters.

2. Experimental procedure

A 5 l semi-batch reactor is fabricated for the study of CO_2 hydrate formation. The experiments are carried out at 2.5–4.5 MPa and 3–8 °C to study CO_2 hydrate formation in saline and Persian Gulf waters. Temperature control is achieved by circulating ice water inside a coil in the reactor. The ice water is prepared in a separate refrigeration system and is circulated through the internal coil of the reactor by a pump. The operating conditions of the reactor are monitored by two temperature sensors (PT−100) and two pressure sensors. An interface is developed to transmit sensors' data to the computer. The experimental setup is shown in Fig. 1.

Deionized water and sodium chloride are used for preparing different solutions of saline waters with 5.0–30.0 g/l dissolved sodium chloride. In addition to these synthetic solutions, Persian Gulf water is used as a real solution in the experiments. Carbon dioxide with purity more than 99.9% is used as the hydrate former in all experiments. The used materials and solutions in the experiments are shown in Table 1.

The experiments are carried out by filling the reactor with water and injecting CO_2 until the pressure of 2.5–4.5 MPa is achieved. Temperature is equal to 20 °C

Fig. 1. Experimental setup of CO_2 hydrate formation (1) CO_2 storage tank, (2) ice water batch, (3) hydrate reactor, (4) CO_2 intermediate storage tank, (5) ice water pump, (6) refrigeration system.

Table 1
Properties of carbon dioxide and the aqueous phase

Components	Properties
Deionized water	Conductivity less than 10 μS
Sodium chloride	Purity more than 99.5%
Carbon dioxide	Purity more than 99.9%
Saline water	5, 10, 15, 20, 30 g/l dissolved NaCl
Persian Gulf water	50 g/l dissolved solids

in the beginning of the operation which is higher than the equilibrium hydrate formation temperature at these pressures. At these conditions, the reactor is progressively cooled at a fixed pressure to temperature of 3–8 °C for each runs to enter the hydrate formation zone. After a few minutes of entering the zone, the induction period is started for the formation of a stable nucleus which must be passed to start the growth. The required time to pass the induction period is called the induction time. Afterward, the hydrate formation is continued, reducing the reactor pressure due to CO_2 consumption. To overcome the pressure loss, CO_2 is injected to fix the reactor pressure at the experimental values of 2.5–4.5 MPa. At the mentioned operating conditions, the process of hydrate formation is monitored by calculating the CO_2 consumption.

The consumption is calculated based on the gas law via temperature, volume and pressure loss of CO_2 in the storage tank, connecting pipe and free volume of the reactor. At any time step of the experiment the gas consumption is calculated by Eq. (1).

$$\Delta n = \left(\frac{PV}{ZRT}\right)_{t+\Delta t} - \left(\frac{PV}{ZRT}\right)_{t} \tag{1}$$

In the above equation, P, T and V are pressure, temperature and volume of the storage tank, connecting pipe and free volume of the reactor. Z is the compressibility factor and is calculated by SRK equation of states [21].

After completion of the hydrate formation, the remaining brine is discharged from the reactor and hydrate crystals are allowed to melt. Hydrate crystals are decomposed to carbon dioxide and water. The carbon dioxide is discharged from the reactor and water is gathered in a sampling vessel. One hundred cubic centimeter of water is dried in an oven at 100 °C to measure its solid contents. The measured solid's weight is multiplied to 10 to give the concentration of the dissolved solid in gram per liters of final products. The separation efficiency is calculated by the following equation based on the concentration of the dissolved solids in the water before and after the hydrate formation.

$$\eta = 100\left(\frac{DS_i - DS_f}{DS_i}\right) \tag{2}$$

3. Results

Twenty experiments are carried out at 3–8 °C and 2.5–4.5 MPa to study and compare CO_2 hydrate formation in saline and Persian Gulf waters. A sample of the produced hydrate crystals which is allowed to melt is shown in Fig. 2. The equilibrium hydrate formation pressures are calculated based on the method expressed in [22] at experimental temperature and the water salinity. The equilibrium hydrate formation pressures are shown in Table 2. The salinity of the produced water from decomposed hydrate is measured and shown in the last column of Table 2.

Fig. 2. Decomposing CO_2 hydrate crystal.

CO_2 hydrate crystals are formed in experiments 1–5 at 5.2–8.1 °C and 3.0–4.0 MPa in the presence of saline water with 30 g/l dissolved NaCl. Calculated equilibrium hydrate formation pressures in these temperatures are from 2.67 to 3.94 MPa. Separation efficiencies are calculated by Eq. (2) and are from 3.3% to 24.3%.

Hydrate formation experiments (6–8) are followed with saline water with 20 g/l dissolved NaCl at 5.0–8.5 °C and 3.0–4.0 MPa. Calculated equilibrium hydrate formation pressures in these temperatures are from 2.47 to 3.91 MPa. Separation efficiencies are calculated by Eq. (2) and are from 40.5% to 50.5%.

Experiments 9–13 are carried out with saline water with 15 g/l dissolved NaCl at temperatures of 3.0–8.0 °C and pressures of 2.0–4.0 Mpa, respectively. Calculated equilibrium hydrate formation pressures in these temperatures are from 1.90 to 3.53 MPa. Separation efficiencies are calculated by Eq. (2) and are from 6.7% to 31.3%.

Hydrate formation experiments (14–16) are followed with saline water with 10 g/l dissolved NaCl at 6.0–7.3 °C and 3.0–3.5 MPa. Calculated equilibrium hydrate formation pressures in these temperatures are from 2.65 to 3.12 MPa. Separation efficiencies are calculated by Eq. (2) and are from 18.0% to 41.0%.

Hydrate formation experiments (17–19) are followed with saline water with 5.0 g/l dissolved NaCl at 6.0–7.2 °C and 3.0–3.7 MPa. Calculated equilibrium hydrate formation pressures in these temperatures are from 2.58 to 3.00 MPa. Separation efficiencies are calculated by Eq. (2) and are from 34.0% to 52.0%.

Table 2
The overall results of CO_2 hydrate formation experiments

η (%) Eq. (2)	Salinity of final water (g/l)	Pressure (MPa)		Temperature (°C)	Salinity of initial water (g/l)	No.
		Operating	Equilibrium			
16.7	25.0	3.5 ± 0.05	3.07	6.3 ± 0.5	30	1
3.3	29.0	3.0 ± 0.05	2.67	5.2 ± 0.5	30	2
24.3	22.7	3.0 ± 0.05	2.95	6.0 ± 0.5	30	3
33.7	19.9	3.5 ± 0.05	2.95	6.0 ± 0.5	30	4
23.3	23.0	4.0 ± 0.05	3.94	8.1 ± 0.5	30	5
40.5	11.9	4.0 ± 0.05	3.91	8.5 ± 0.5	20	6
46.5	10.7	3.0 ± 0.05	2.79	6.0 ± 0.5	20	7
50.5	9.9	3.0 ± 0.05	2.47	5.0 ± 0.5	20	8
20.0	12.0	2.0 ± 0.05	1.90	3.0 ± 0.5	15	9
6.7	14.0	3.0 ± 0.05	2.40	5.0 ± 0.5	15	10
30.0	10.5	4.0 ± 0.05	3.30	7.5 ± 0.5	15	11
31.3	10.3	4.0 ± 0.05	3.53	8.0 ± 0.5	15	12
34.7	9.8	4.0 ± 0.05	3.17	7.2 ± 0.5	15	13
41.0	5.9	3.0 ± 0.05	2.65	6.0 ± 0.5	10	14
18.0	8.2	3.5 ± 0.05	3.04	7.1 ± 0.5	10	15
27.0	7.3	3.5 ± 0.05	3.12	7.3 ± 0.5	10	16
34.0	3.3	3.0 ± 0.05	2.58	6.0 ± 0.5	5	17
52.0	2.4	3.0 ± 0.05	2.74	6.5 ± 0.5	5	18
20.0	4.0	3.7 ± 0.05	3.00	7.2 ± 0.5	5	19
57.1	21.0	3.0 ± 0.05	2.27	3.0 ± 0.5	PGW*	20

*PGW: Persian Gulf water with 49 g/l total dissolved solid

Hydrate formation experiment (20) is followed with Persian Gulf water with 49 g/l total dissolved solid at 3.0 °C and 3.0 MPa. Calculated equilibrium hydrate formation pressure in this temperature is equal to 2.27 MPa. Separation efficiencies are calculated by Eq. (2) and are equal to 57.1%.

4. Conclusion

CO_2 hydrate formation is studied experimentally in the presence of saline water and Persian Gulf water to investigate simultaneous CO_2 capture and water desalination. Hydrate formation rate in the growth stage is high enough to form quickly the hydrate when contacting carbon dioxide and water for all experiments which hydrate formation is observed.

When hydrate formed it can be stored in a safe place and transported to other places for beneficial usages. Decomposed hydrate produces carbon dioxide and water which are vital for plants growth in green houses and micro algae farms. Micro algaes have found widespread usages such as biodiesel and protein productions.

Symbols

DS — Dissolved solid (g/l)
Δn — CO_2 consumption (mole)
P — Pressure (MPa)
R — Gas constant (MPa m^3/kmol K)
t — Time (s)
Δt — Time step (s)
T — Temperature (°C)
V — Volume (m^3/kmol)
Z — Compressibility factor
η — Separation efficiency

Acknowledgements

Authors greatly acknowledge financial support of the office of Basic Research and Applied Studies of Planning, Development and Research Deputy of the Ministry of Industries and Mines. Also the cooperation of Fars ERC to give the permission to publish the data is acknowledged.

References

[1] K.Z. House, D.P. Schrag, C.F. Harvey and K.S. Lackner, PNAS, 103 (2006) 12291–12295.
[2] E.D. Sloan, Clathrate Hydrates of Natural Gases, M. Dekker, 1998.
[3] M. Sarshar and J. Fathikalajahi, Kinetics study of CO_2 hydrate formation in saline water, in: 1st Conference on Chemical Engineering and Advanced Materials (CEAM), 2009, Naples, Italy.

[4] H.J. Lee, J.D. Lee, P. Linga, P. Englezos, Y.S. Kim, M.S. Lee and Y.D. Kim, Energy, 35 (2010) 2729–2733.
[5] R. Kumar, P. Linga, J.A. Ripmeester and P. Englezos, J. Environ. Eng., 135 (2009) 411–417.
[6] M.Sarshar, F. Esmaeilzadeh and J. Fathikaljahi, Chem. Eng. Commun. 196 (2009) 1348–1365.
[7] G. Ersland, J. Husebø, A. Graue and B. Kvamme, Energy Procedia, 1 (2009) 3477–3484.
[8] P. Szymcek, S.D. McCallum, Patricia Taboada-Serrano and C. Tsouris, Chem. Eng. J., 135 (2008) 71–77.
[9] C. Tsouris, S. McCallum, D. Aaron, D. Riestenberg, J. Gabitto, A. Chow and E. Adams, AIChE J., 53 (2007) 1017–1027.
[10] N.H. Duc, F.Chauvy and J.M. Herri, Energy Conver. Manage., 48 (2007) 1313–1322.
[11] P. Linga, A. Adeyemo and P. Englezos, Environ. Sci. Technol., 42 (2008) 315–320.
[12] P. Linga, R. Kumar and P. Englezos, Chem. Eng. Sci., 62 (2007) 4268–4276.
[13] P. Linga, R. Kumar and P. Englezos, J. Hazard. Mater., 149 (2007) 625–629.
[14] T. Buanes, B. Kvamme and A. Svandal, J. Cryst. Growth, 287 (2006) 491–494.
[15] N. Goel, J. Petroleum Sci. Eng., 51 (2006) 169–184.
[16] B. Kvamme, A. Graue, T. Buanes, T. Kuznetsova and G. Ersland, Int. J. Green House Gas Cont., 1 (2007) 236–246.
[17] S.P. Kang and H. Lee, Environ. Sci. Technol., 34 (2000) 4397–4400.
[18] M. Sarshar and M. Bonyadi, First International Conference on SeaWater Desalination, Olympics Hotel, Tehran, 2007.
[19] J. Javanmardi and M. Moshfeghian, Appl. Thermal Eng., 23 (2003) 845–857.
[20] R.A. McCormack and R.K. Andersen, Clathrate Desalination Plant, Preliminary Research Study, US Department of the Interior, Bure.au of Reclamation Technical Service Center, Water Treatment Engineering and Research Group, Water Treatment Technology, Program Report No. 5, 1995.
[21] G. Soave, Chem. Eng. Sci., 27 (1972) 1197–1203.
[22] W.R. Parrish and J.M. Prausnitz, Indust. Eng. Chem. Process Design Develop., 11 (1972) 26–35.